THE TRIPLET STATE AND MOLECULAR ELECTRONIC PROCESSES IN ORGANIC MOLECULES

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I. INTRODUCTION

A. HISTORICAL

The first identification of a spectroscopic phenomenon with the triplet level of an organic molecule was made in 1937 by Sklar (366), who observed a weak absorption system in the 3400-A region of benzene and assigned it to a singlet–triplet intercombination on the basis of its feeble intensity. Prior to this, Jabłoński (170) had suggested an energy-level scheme to explain phosphorescence, a phenomenon that had been extensively studied by Vavilov and Levshin (396), Kowalski (203a), and others. Phosphorescence was presumed to represent the direct radiative decay of a "metastable state" that is situated somewhat below the energy of the "normal," "labile," or fluorescent (excited singlet) state. The relation between the wavelengths of Sklar's absorption and the known phosphorescence spectrum of benzene was evidently not noticed. In 1941 Lewis, Lipkin, and Magel (221) suggested that the characteristic absorption spectra of phosphorescing molecules (T–T absorption) might be due to triplet excitation, but the authors were unable to distinguish between this possibility and some type of molecular tautomerism. In 1943–1944 Terenin (391) pointed out the similarity between phosphorescence and the well-characterized multiplicity-forbidden transitions of atomic systems, and suggested the involvement of a triplet biradical. Independently in 1944, Lewis and Kasha (218) published their widely cited paper identifying phosphorescence as radiative intercombination between the lowest triplet excited state and the (singlet) ground state, and shortly thereafter Lewis and Calvin (216, 217) demonstrated the existence of unpaired electrons in the phosphorescent state. Weissman and Lipkin (400) established the electric dipole nature of phosphorescence (in fluorescein), eliminating the possibility that the long-lived emission is a result of a (less probable) electric quadrupole or magnetic dipole transition. That a spin–orbital coupling process is responsible for intercombinations involving the metastable state was shown by the heavy-atom substituent perturbation experiments of McClure (240); this effectively proved the triplet character of the phosphorescent state, and Hutchison and Mangum's characterization of the triplet state of naphthalene by electron spin resonance studies provided a final answer to the question (163, 164).

B. EXCITATION AND DEACTIVATION OF THE LOWEST TRIPLET STATE

1. *Excitation of the Triplet State*

The extremely low absorption coefficients associated with $S_0 \rightarrow T_1$ transitions make the *direct excitation* of the triplet state a very inefficient process; however, it can be achieved by the use of sufficiently intense radiation (8, 331) and is of current interest in connection with laser-excitation studies (138, 197).

Population of the triplet state is ordinarily accomplished by excitation to an upper level of the singlet manifold, permitting full utilization of the available incident light by one or more of the intense absorption bands associated with $S_1 \leftarrow S_0$ transitions. Rapid intramolecular conversion and transfer processes then render a portion of the excited molecules into their triplet states. In rigid-medium studies, triplet population can be successfully achieved by steady-state illumination. In fluid medium a high-intensity lamp is required, owing to the relatively short lifetime of the triplet state. A recent elaboration of this method is the high-intensity flash technique developed by Norrish (267), Porter (294), and Ramsay (316).

Triplet-excited states can result from the recombination of an electron with an ionized molecule (35, 215, 227). Initial formation of the ion-electron pair or radicals can be accomplished by sufficiently energetic light, pulsed electron beam irradiation, γ- or X-ray irradiation (246), or through chemical reactions. These processes are of particular interest in radiation-damage studies.

Thermal population of the triplet state is readily accomplished in dianthrone [9,9′-diketo-9,9′-dianthracene], which has a relatively low-lying triplet state. Yellow solutions of this substance become green on heating, an example of *thermochromism.* The change of color is presumably due to triplet–triplet absorption.

Excitation by *intermolecular energy transfer* from a higher triplet or singlet state is responsible for *sensitized phosphorescence* and other phenomena that are discussed elsewhere in this article.

2. *Modes of Triplet Decay*

Figure 1 is a modern elaboration of Jabłoński's diagram (170), representing the energies of the various low-lying states of a typical aromatic hydrocarbon molecule with respect to the ground state S_0. The two sets of vibronic states based on S_0, S_1, S_2 and T_1, T_2 constitute the singlet and triplet manifolds, respectively; transitions of the system between states of different manifolds are known as *intercombinations* and, in accordance with the multiplicity-forbiddeness selection rule, are ordinarily less probable by a factor of $\sim 10^{-6}$ than symmetry- and spin-allowed transitions that are confined to either manifold (184).

The various electronic transitions are classified as radiative or radiationless, represented in Figure 1 by solid and broken lines, respectively. In *radiationless transitions*, the excess electronic excitation is converted directly into heat. This process is generally known as internal conversion when it occurs between states of the same manifold, whereas the radiationless $S_1 \rightarrow T_1$ intercombination is called *intersystem crossing* (184). Internal conversion from the lowest emitting levels (S_1 or T_1) to the ground state, particularly when brought about by the action of another molecule, is often known as *quenching.* Internal conversions connecting upper states with the lowest *excited* level of the same manifold are very rapid (k_{IC} = 10^{10}–10^{13} sec^{-1}), as can be deduced from the fact that radiative emission (occurring at a maximum rate of 10^9 sec^{-1}) is only observed from the lowest excited level of a given multiplicity, and must therefore be in competition with a radiationless process that is at least 10^3 times faster. The factor of 10^3 reflects an experimental limitation—it is not ordinarily practical to measure light intensities that are weaker than commonly encountered luminescent materials by a larger factor than 10^3. However, using sensitive apparatus, Parker and Hatchard (277) have succeeded in measuring Φ_P/Φ_F ratios of $<10^{-5}$. With this type of apparatus, studies on the ratio of the emission from higher excited singlet levels to that from the lowest singlet level should be possible, and the rate of deactivation of higher excited singlet states can accurately be determined.

From the line width of absorption in rare gas matrices, Robinson (321) estimates the lifetime for the vibronic levels of the second excited state of naphthalene to be longer than 10^{-11} sec.

Radiative transition between two states of identical multiplicity is known as *fluorescence;* only $S_1 \rightarrow S_0$ fluorescence is observed, as a consequence of the very high rate of radiationless conversion between (closely spaced) excited states. Emission from the lowest triplet state to the ground state ($T_1 \rightarrow S_0$) is called *phosphorescence* (184). The "reverse" intersystem-crossing process ($S_1 \leftarrow T_1$) frequently occurs when the S_1 and T_1 states are energetically similar and the lifetime of the latter is sufficiently long; thermal excitation of a molecule already in its triplet state (frequently possible even below room temperature) results in intersystem crossing and emission corresponding to the normal fluorescence in the spectrum but of much longer lifetime as a result of the sojourn of the excitation in the long-lived triplet state. This emission is a form of delayed fluorescence which we call *α-delayed fluorescence,* or (in honor of the older but misleading term) *α-phosphorescence.*

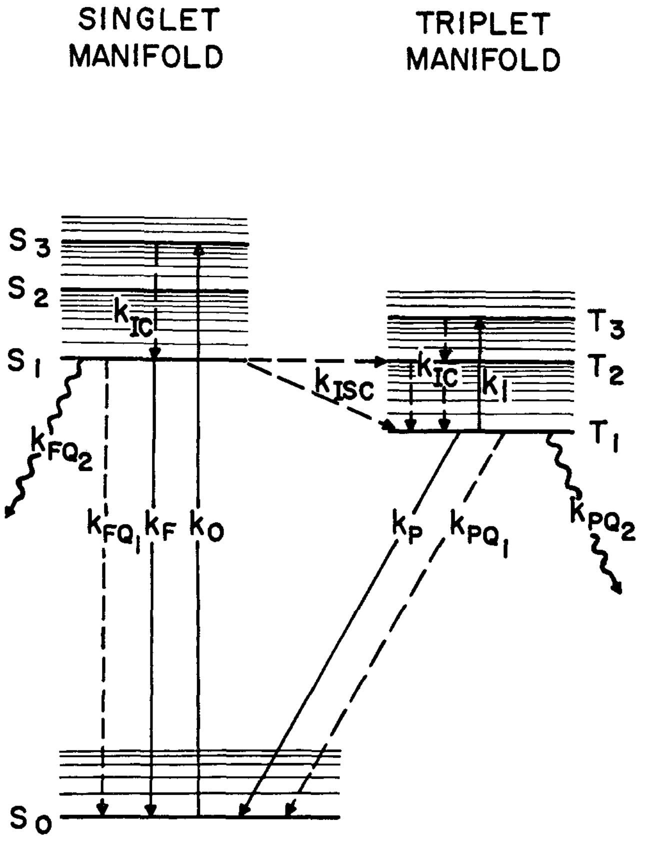


Figure 1.—Pathways of triplet excitation and decay. Solid arrows represent radiative processes, corresponding to absorption or emission of light. Dashed and wiggly lines denote nonradiative unimolecular and bimolecular processes, respectively. See text for definitions of the various rate constants.

Many of these terms were in use long before the origins of the emission were understood, with the unfortunate consequence that they were applied according to some property of the emission (*e.g.*, lifetime or wavelength) which does not always accurately reflect its true nature. Thus other frequently encountered terms for *phosphorescence* are "β-phosphorescence," "delayed fluorescence," and "long wavelength phosphorescence" or "-luminescence"; *α-delayed fluorescence* is also called α-phosphorescence, "phosphorescence" (304), and "short-wave phosphorescence." These other terms are found in much of the older (pre-1950) literature, as well as in some Soviet and most Polish papers, and result in much confusion to users of abstracts and indexes; sometimes the type of emission under discussion can only be learned from the context or from prior knowledge of the properties of the material being studied.

Other causes of delayed fluorescence are radical and ion recombinations and triplet–triplet annihilative processes. Current intense interest in the latter subject has led to the use of the term *delayed fluorescence* to describe $S_1 \rightarrow S_0$ emission resulting from triplet–triplet interaction, in the absence of any further qualification. Very slow electron–ion recombination processes in rigid media sometimes give rise to *delayed phosphorescence* (227) which may last for as long as an hour (215).

Triplet–triplet interaction, mentioned above, and radiationless *intermolecular T → T or T → S transfer* are very important routes of triplet deactivation, particularly in fluid and solid solutions.

Triplet–triplet absorption is a mode of triplet deactivation, especially at high light intensities, and particularly when the process is followed by a photoreaction or photodecomposition. The photodecomposition of rigid solvents containing naphthalene has been explained in terms of absorption of a photon by T_1 followed by transfer of energy from a higher triplet state to the solvent (358).

In liquid solution, bimolecular (or pseudo-unimolecular) quenching by molecular oxygen or other impurities is the most probable fate of triplet-excited molecules.

Förster's (117) discussion of the kinetics of fluorescence and phosphorescence is limited to cases of low triplet concentrations and low intensity of exciting light so that triplet–triplet annihilation and triplet–triplet absorption need not be considered. The following equations were derived.

$$\text{Singlet decay } \frac{d[S]}{dt} = -(k_F + k_{FQ} + k_{ISC})[S] + k_\alpha[T] + k_0[S_0] \quad \text{(Eq 1)}$$

$$\text{Triplet decay } \frac{d[T]}{dt} = -(k_P + k_{PQ} + k_\alpha)[T] + k_{ISC}[S] \quad \text{(Eq 2)}$$

$$\text{Quantum yields } \Phi_F = \frac{k_F}{k_F + k_{FQ} + k_{ISC}}$$

$$\Phi_P = \frac{k_P k_{ISC}}{\lambda} \quad \text{(Eq 3)}$$

$$\Phi_\alpha = \frac{k_F k_{ISC} k_\alpha}{(k_F + k_{FQ} + k_{ISC})\lambda}$$

Observed lifetimes (not natural or radiative)

$$1/\tau_F = k_F + k_{FQ} + k_{ISC} \quad \text{(Eq 4)}$$

$$1/\tau_P = k_P + k_{PQ} + k_\alpha \frac{k_F + k_{FQ}}{k_F + k_{FQ} + k_{ISC}} \quad \text{(Eq 5)}$$

where $k_{PQ} = k_{PQ_1} + k_{PQ_2}$, k_{PQ_1} being the rate constant of unimolecular $T_1 \rightarrow S_0$ quenching, and $k_{PQ_2} = k'_{PQ_2}[Q]$, where k'_{PQ_2} is the rate constant of bimolecular quenching by another substance Q. A similar definition of $k_{FQ} = k_{FQ_1} + k_{FQ_2}$ is applicable to the fluorescence process

$$\lambda = (k_F + k_{FQ} + k_{ISC})\,(k_P + k_{PQ} + k_\alpha) - k_{ISC}k_\alpha$$

and $k_\alpha{}^{(T)} = k_\alpha{}^\circ e^{-\Delta E/R\tau}$; k_α (the rate of the $T_1 \rightarrow S_1$ process) and k_{PQ_2} can be neglected at low temperatures. Thus

$$\frac{1}{\tau_P} = k_P + k_{PQ_1} \quad \text{(Eq 6)}$$

In fluid solution, bimolecular (often pseudo-unimolecular) quenching due to impurity species is ordinarily the most active route of triplet depopulation. In dilute rigid medium, phosphorescence quenching is mainly due to the unimolecular $T_1 \rightarrow S_0$ radiationless process [PQ_1].

Kinetic schemes for calculating values of these rate constants from experimental data have been given by Koizumi and Kato (202), Gilmore and Lim (125), and Aristov and Sveshnikov (7).

Since phosphorescence must compete with nonradiative decay processes that are in general very rapid, it is necessary to distinguish between the *observed* phosphorescence lifetime τ_P and the radiative or *natural* lifetime $\tau_0 = 1/k_P$, that would presumably be observed in the absence of all quenching processes (*i.e.*, when $k_{PQ} = k_\alpha = 0$ in Eq 5) and is an inherent property of the molecule. It is sometimes estimated from the intensity of singlet → triplet absorption, to which it can be related through the expression $\tau_0 = 1.5/f(\bar{\nu})^2$ sec, where f is the oscillator strength and $\bar{\nu}$ is the center frequency of the absorption band in wavenumber, or equivalently (see ref 201)

$$k_P = \frac{1}{\tau_0} = \frac{(\bar{\nu})^2}{3.47 \times 10^8} \frac{g_1}{g_u} \int \epsilon d\bar{\nu}$$

where $\bar{\nu}$ is an average frequency for the molecular transition, and g_1 and g_u are degeneracies of the lower and upper states, respectively. The question concerning g_u for the triplet state has recently been raised (321). Because of spin–orbit selection rules, the probability of transition to all three sublevels is not equal, and for aromatic molecules the transition probability can be equivalent to two of the three sublevels at the most. Thus $g_u = 1$ or 2 but never 3 as has been previously assumed. The above formula is for a resonance transition. For strongly allowed molecular transitions, the formula has been modified recently by Strickler and Berg (381).

3. Types of Molecular Electronic Transitions

A molecular electronic state can be described in terms of the appropriate electronic configuration and electron distribution. These, in turn, are expressed in terms of one-electron electronic wave functions which can be found by valence-bond or molecular-orbital methods; in practice, the latter method has proved to be more convenient in discussing unsaturated systems.

Figure 2 shows orbital diagrams and electronic configurations for the σ, π, and n (nonbonding) orbitals for pyridine in its ground state and several different excited states. Rydberg transitions (in which the principal quantum number changes) are not indicated since they are located in a less easily accessible energy range and have not been as carefully studied as the lower sub-Rydberg states. Transition I, known as an (n,π^*) transition, occurs in compounds containing heteroatoms. Transition II is of (π,π^*) type and occurs in all unsaturated compounds. Transitions III and IV are of (π,σ^*) and (σ,σ^*) types, respectively, and can be observed in the vacuum ultraviolet region.

C. SIGNIFICANT RECENT ADVANCES

In recent years, a number of workers, specialized formally in a variety of fields, have devoted much study to the lowest triplet state of unsaturated molecules. Phosphorescence spectroscopy has probably been the most useful tool, and recently developed methods of obtaining high-resolution "linelike" molecular emission spectra have provided important information on triplet assignments and configurations. Polarization studies have added to our understanding of the emission process. Magnetic resonance experiments have left little doubt about the triplet nature of the phosphorescent state. Qualitative theories of radiationless processes have been proposed, and have stimulated further experiments on quantum yields and activation energies, as well as the effects of environment on lifetimes. Mechanisms for the inter- and intramolecular heavy-atom effects have been proposed. The shapes of molecules in the triplet state have been studied both by esr and optical methods. From esr studies in single crystals the electron distribution and symmetry of aromatic molecules in the excited triplet state in host crystals has been calculated. Energy transfer from and to the triplet state has been examined and demonstrated by spectroscopic, chemical, and esr methods.

The triplet state is of great photochemical interest. Both the relatively long lifetime (even in fluid medium) and the presence of the two unpaired electrons makes this state a reactive species. In the past few years, the energies of triplet states for some nonphosphorescent molecules have been successfully determined by "chemical spectroscopy"; using triplet–triplet transfer processes followed by chemical changes in the acceptor, one can determine the transfer efficiency as well as the relative positions of the triplet states of different donors and acceptors. Studies on triplet–triplet absorption in fluid media have been especially fruitful and have provided much kinetic data on the quenching process of the triplet state. Polarization studies on T–T absorption in rigid glasses and crystalline media have been carried out and have permitted an assignment of these transitions in some aromatic systems.

The existence of triplet excitons has been proved, and they have been shown to have a longer diffusion length than singlet excitons in organic crystals. Triplet–triplet annihilation, a new effect involving triplet states of polyatomic molecules, has been discovered. This interaction gives rise to fluorescence which has a lifetime that is determined by the rate at which the triplet molecules interact. These processes have been found in gases, liquids, glasses, and crystals.

$T_1 \leftarrow S_0$ absorption has been observed by means of external-perturbation enhancement, using heavy-atom solvents as well as O_2 and NO; theories on the cause of this enhancement have been proposed. Magnetic rotation experiments have detected $T_1 \leftarrow S_0$ absorption for several heterocyclics and ketones.

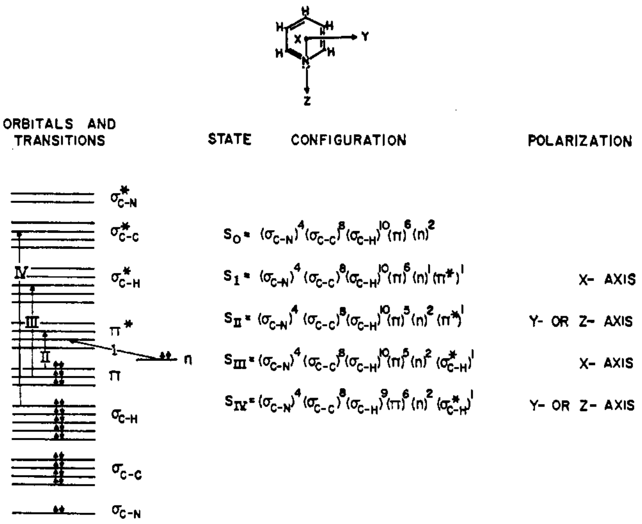


Figure 2.—Electronic orbitals, states, and transitions for pyridine.

An indirect method of measuring $T_1 \leftarrow S_0$ absorption in crystals has been demonstrated, in which the activation curve for the formation of the triplet state is determined by using exciting light in the $T_1 \leftrightarrow S_0$ absorption region and observing either phosphorescence or the delayed fluorescence that results from triplet–triplet interaction.

This review specifically covers the period of 1956–1964 and is concerned only with the lowest *excited* (not ground) triplet state. The topic has been previously reviewed by Kasha and McGlynn (189) and by Reid (319). Because of the immense literature on the subject, it is impractical to discuss every paper which has appeared in the field. Some specific areas have been carefully reviewed previously and therefore only the important developments in these areas are covered here. Because of the extensive development of the field of "triplet-state photochemistry," no attempt has been made to discuss this topic. Workers interested in a certain specialized area of the field are referred to the references given in Table I.

II. Intramolecular Singlet–Triplet Radiationless Processes

A. THEORIES OF RADIATIONLESS TRANSITIONS IN RIGID MEDIA

Only recently have we achieved even a qualitative understanding of radiationless transitions, but this has already led to the development of theoretical explanations of these processes, in spite of the dearth of accurate and quantitative data on quantum yields.

Two theories of radiationless transitions have been independently developed (131, 326, 327); they differ formally from one another in the origin of the perturbation. The final results differ mainly in the predicted

TABLE I

SUGGESTED ARTICLES ON TOPICS RELATED TO THE TRIPLET STATE

Topic	Authors	Ref
1. Organic photochemistry	"Advances in Photochemistry," Vol. I, II, and III	268
	Livingston	235
	Hochstrasser and Porter	154
2. Luminescence in crystals	Windsor	407
	Hochstrasser	155
3. Excitons	Davydov	58
	Knox	201
	Kasha	186
	Hochstrasser	155
	McClure	243
	Craig and Walmsley	51
Triplet excitons	Jortner, Rice, Katz, and Choi	173
4. Energy transfer		
a. Theoretical considerations	Förster	116, 120
	Kasha	184, 187
	Dexter	61
	Livingston	236
Triplet–triplet	Ermolaev	96
b. In biological systems	*Radiation Res. Suppl.*, **2** (1960).	
	Discussions Faraday Soc., **27** (1959)	
	Rabinowitch	314
	Reid	318
c. In photosynthesis	Robinson	323
d. Radiationless transitions in fluid media	Seybold and Gouterman	342
5. n,π^* transitions	Sidman	356
	Goodman	126
	Kasha	188
6. Electronic spectroscopy techniques	Robinson	322
	Parker and Hatchard	276a
7. Esr studies		
a. In crystals	Hutchison	161
b. In glasses	de Groot and van der Waals	134
c. In biology	Smaller	367
8. Triplet-state symmetry assignments	Kearns	192

temperature effects on the radiationless transition probability.

1. *The Phonon Field Theory*

Gouterman (131) has treated semiclassically the problem in which the vibronically (vibrational-electronic) excited molecule interacts with the time-dependent oscillatory phonon field. The treatment follows that previously given for the interaction of molecular systems with the photon field. According to this treatment, the transition probability k for the radiationless process between two levels m and n is given by

$$k_{\mathrm{emission}}\ \alpha \left[\frac{4\omega^3}{3\hbar C_s^{\,3}}\right] |\vec{\mathrm{M}}_{\mathrm{mn}}{}^{s}|^2 \times \left[1 + \left[e^{\frac{h\nu}{2\pi kT}} - 1\right]^{-1}\right] \quad \text{(Eq 7)}$$

$$k_{\mathrm{absorption}}\ \alpha \left[\frac{4\ \omega^3}{3\hbar C_s^{\,3}}\right] |\vec{\mathrm{M}}_{\mathrm{mn}}{}^{s}|^2 \times \left[e^{\frac{h\nu}{2\pi kT}} - 1\right]^{-1} \quad \text{(Eq 8)}$$

where $\omega/2\pi c = E_{\mathrm{m}} - E_{\mathrm{n}}$ in cm^{-1}, C_s = velocity of sound, and $\vec{\mathrm{M}}_{\mathrm{mn}}{}^{s}$ is the matrix element connecting the two states. It is composed of a product of the vibrational overlap factors and the electronic matrix elements. The latter is not confined to the dipole term; Gouterman showed that higher terms could be equally important.

According to this theory, emission of phonons occurs if the final molecular state is below the initial molecular level and absorption occurs if the final level is above the initial level. Gouterman shows that to the first approximation, only single phonon processes are involved. The necessity of extending this theory to include the possibility of nonlinear interactions in the phonon coordinates that would allow multiphonon processes has been indicated (137). The above equations show the high dependence of the transition probability of radiationless processes (especially phonon absorption) on temperature.

2. *The Time-Independent Theory*

Robinson and Frosch (326, 327) have developed a theory in which time-independent perturbations, caused by the relatively small Coulombic terms such as spin–orbit interaction, connect zero-order nonstationary states of the molecular system. The effect of the lattice is to increase the density of final states when it is coupled to the molecular vibronic levels. The crowded lattice vibronic levels enable the initial and final states to be in close resonance, thus increasing their interaction. The transition is envisioned to occur as a result of weak, time-independent coupling of the initial level to a near-resonance band of strongly coupled final states. Once the transition to the quasi-continuum of final states occurs, fast vibrational relaxation prevents the back transition to the initial state. Their expression for the radiationless transition probability is given by

$$k_{\mathrm{I,II}} = \frac{8\pi^2\tau}{h^2}\ \left|\mathrm{i,j}\,\langle\Theta_{\mathrm{Ii}}\Theta_{\mathrm{IIj}}\rangle^2\langle\Phi_{\mathrm{I}}|\mathcal{H}'|\Phi_{\mathrm{II}}\rangle^2 \quad \text{(Eq 9)}$$

where Θ_i and Θ_j are the vibrational wavefunctions belonging to the two different electronic states Φ_{I} and Φ_{II}, respectively, and τ is the vibrational relaxation time. $\mathcal{H}'$ is a perturbing Hamiltonian; if I and II are singlet and triplet, respectively, then $\mathcal{H}'$ is the spin–orbit coupling operator, and if both have the same multiplicity, then $\mathcal{H}'$ could simply be electron repulsion or the vibronic operator. The vibrational overlap factor is generally much smaller than unity except in the regions of crossing of the potential energy surfaces, where it is equal to unity.

According to Robinson and Frosch's theory, the radiationless transition probability does not strongly depend on temperature. Studies on naphthalene and naphthalene-d_8 (137) show that the $T_1 \rightarrow S_0$ radiationless probability is temperature independent, thus supporting Robinson and Frosch's ideas. However, other recent studies (22a) indicate that the probability of radiationless transitions between $^5D_0$ or $^5D_1$ levels and the ground state of Eu^{3+} in rare earth chelates is temperature dependent while the $^5D_1 \rightsquigarrow {}^5D_0$ transition in the same system is not. Certainly transitions involving the π electrons in naphthalene and those involving the f electrons in Eu^{3+} are expected to behave in a different manner; the strength of their coupling to the environment is of different degree. If the coupling between the molecule or ion and its environment is so weak during the transition that the phonon field would strengthen it, then the rate of the radiationless process would be determined by the strength of the phonon perturbation (and therefore should be temperature dependent). If, on the other hand, the coupling is already strong, then the rate at which the molecule changes its degree of excitation in its medium would determine the rate of the radiationless process.

A significant recent experiment by Williams and Goldsmith (406a) indicates that, in tetracene vapor, radiationless transition from the second excited singlet state (S_2) to an accidentally degenerate vibronic level of S_1 occurs at very low pressures, when the period between collisions is much longer than the radiative lifetime of the S_2 state. If these results are interpreted correctly, they suggest that radiationless transition in this molecule does not require collisional or phonon interaction, but that it occurs because of intramolecular perturbation (see Figure 3).

In the past few years, few observations have been discussed in terms of the integrals appearing in the expressions for the radiationless transition probability. These results are to be discussed below.

B. RADIATIONLESS TRANSITION SELECTION RULES

1. Vibrational Overlap Integrals and the Rate of the $T_1 \rightarrow S_0$ Transition

Hutchison and Mangum have observed that perdeuterionaphthalene has a phosphorescence lifetime of ~17 sec in rigid medium, *i.e.*, *ca.* eight times longer than that of regular naphthalene. A number of proposals have been put forward to explain this isotope effect on the phosphorescence lifetime; only that of Robinson and co-workers (326, 408) seems to be correct. These workers proposed that the effect is a result of decreased radiationless transition probability in $C_{10}D_8$ (as compared to $C_{10}H_8$) due to the relatively small value of the overlap integral between the zero-point wavefunction of the triplet state and that of the isoenergetic carbon-deuterium vibration modes of the ground state. The overlap integral in Eq 9 is a product over all the different vibrational modes; if the overlap due to the hydrogen modes is different in the two molecules, it is expected that the over-all value of the overlap integral would be different and the rate of the $T_1 \rightarrow S_0$ radiationless process would be altered.

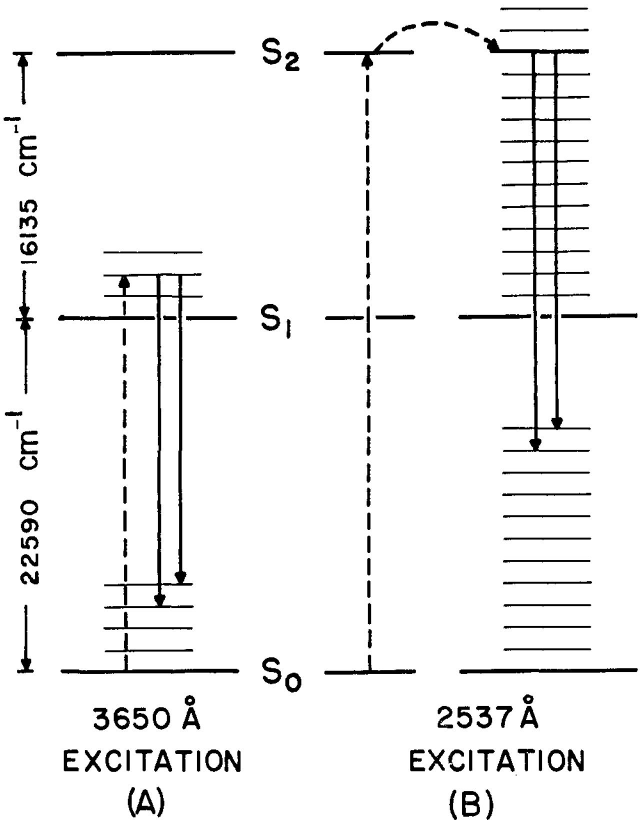


Figure 3.—Excitation of tetracene vapor to its second singlet-excited state is believed to result in rapid conversion to a high vibrational level of S_1, followed by emission from this same level (since the molecule cannot lose energy by collision) to a similarly high level of the ground state S_0 (after Williams and Goldsmith (406a)).

Experiments on rare earth ions have provided further illustration of deuterium effects on lifetimes and intensities of luminescence. Kropp and Windsor (208) noted an increase in both the lifetime and intensity of the visible emission of ions (*e.g.*, Eu^{3+} and Tb^{3+}) in D_2O, as compared to H_2O. These ions are hydrated in solution, and it is presumed that the difference in the overlap factors of the two types of aqua complexes would cause large changes in the rate of radiationless decay. Similarly, Freeman and Crosby (122) have found the luminescence lifetime of crystalline rare earth salts to be greater when the water of hydration is D_2O than when it is H_2O. Substitution of ligand hydrogen atoms by fluorine in several rare earth chelates has also been shown to increase the lifetime and intensity of luminescence. Bhaumik and Nugent (22a) propose that this effect is again a consequence of the small vibrational overlap integral associated with the heavier fluorine atom; however, the difference in

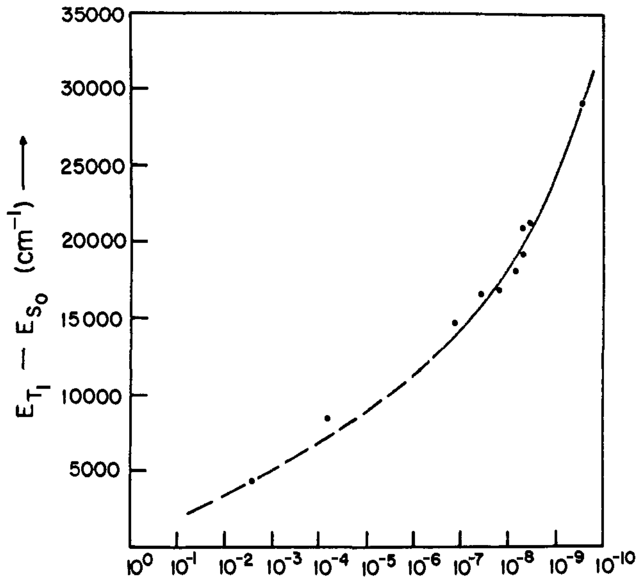


Figure 4.—The dependence of vibrational overlap integral on the energy separation between the lowest triplet and ground states, as calculated by Robinson and Frosch (326).

the electronic structure of H and F makes it difficult to assign this effect entirely to the smaller vibrational factors.

According to Robinson, classical "crossing" of potential energy surfaces is not necessary for radiationless transitions to occur. Tunneling can cause such transitions to take place from one electronic state to the other, especially if the vibrational overlap integral of the two states is not vanishingly small. Of course, at the crossing of the potential surfaces, the overlap factors are equal to unity, and a very high value for the transition probability is expected. The vibrational overlap factors depend upon difference in geometry, differences in vibrational frequencies in the electronic states, size of the molecule, and the energy gap between initial and final electronic states.

As the energy separation between the lowest triplet state and the ground state of a series of aromatic hydrocarbons is decreased, the observed lifetimes of phosphorescence are also found to decrease. Robinson and Frosch (326) explain this trend in terms of an increase in vibrational overlap factors. Assuming an electronic matrix element of 0.01 cm^{-1} for the $T_1 \rightsquigarrow S_0$ transition and using the observed lifetimes, they have calculated the vibrational overlap factors as a function of the energy separation between lowest triplet and the ground state for a series of hydrocarbons (see Figure 4). The authors (326) have extrapolated the overlap factors to unity when $E_T - E_S = 0$ in their paper. This extrapolation is not generally correct, and is justified only for very large, stable molecules, where one-electron excitation does not affect the molecular structure.

Changes in the equilibrium internuclear distance of the excited state relative to the ground state are also expected to affect the vibrational overlap and phosphorescence lifetime, and El-Sayed (75) has suggested this as an explanation for effects of pressure and chemical substitution on observed phosphorescence lifetimes.

El-Sayed (74) pointed out that relatively large differences in the internuclear equilibrium distances between two states can result if the two states arise from transitions of different character, *e.g.*, n,π^* and π,π^* states in heterocyclics. The intersystem radiationless transitions $^1(n,\pi^*) \leftrightarrow {}^3(\pi,\pi^*)$ or $^1(\pi,\pi^*) \leftrightarrow {}^3(n,\pi^*)$ in N-heterocyclics can be $\sim$100 times faster than that between states of the same type (*i.e.*, $^1(n,\pi^*) \leftrightarrow {}^3(n,\pi^*)$ or $^1(\pi,\pi^*) \leftrightarrow {}^3(\pi,\pi^*)$) and separated by the same amount of energy. Recent calculations by Ross (330a) and coworkers indicate that this factor is of the correct order of magnitude; use was made of the theory previously developed by Hunt, McCoy, and Ross (159) which enables calculation of tunneling rates from vibrational overlap factors. This theory treats internal conversion in aromatic hydrocarbons in terms of a single parameter, the root-mean-square change in bond length upon excitation. This parameter may be used to derive a "barrier" distance between the two states between which the radiationless transition is occurring. Pariser's wavefunction was used for the calculations; empirical relations were applied to obtain the required bond lengths in the different excited states. A zero value for the barrier distance corresponds to a crossing of the potential energy surfaces. A prohibition factor of 10^{-6} was selected for the electronic part of S–T radiationless transitions (as compared to internal conversion).

2. The Electronic Integral and the Intersystem-Crossing Process

The radiationless transition probability is proportional to the square of the expectation value of the perturbing operator connecting the two states between which the transition is occurring. For transitions between states of different multiplicity, spin–orbit perturbation is required. It is interesting to point out that in aromatic molecules like benzene, naphthalene, and anthracene, spin–orbit mixing between the lowest excited triplet state and the ground state is vanishing to the first order. Transitions to vibronic levels of the ground state of symmetry A_u, B_{1u}, B_{2u}, or B_{3u} are spin-orbitally allowed. This means that the $T_1 \rightarrow S_0$ radiationless transition is allowed in the second order (326).

Nitrogen heterocyclics possess both n,π^* and π,π^* transitions; in small ring compounds, the lowest singlet state is of the n,π^* type. Most of these molecules show no fluorescence but have strong phosphorescence. This behavior cannot be due to the small radiative power of the n,π^* transition since some n,π^* singlet–singlet transitions have an intensity comparable to the lowest transition in benzene, which shows both fluorescence and phosphorescence.

El-Sayed (76) has shown that to the first order, spin–orbit coupling is forbidden between states of the same configuration. Since in monoazines both singlet and triplet n,π* states belong to the same configuration, it is concluded (76) that intercombinations between n,π* states are forbidden to the first order in these compounds. It was also shown that in polyazines, spin–orbit interaction between n,π* states of different configurations vanishes to the first order (76). McClure (242) had previously shown that spin–orbit interaction between π,π* states is vanishingly small due to the vanishing one- and two-center terms. Combining these results, El-Sayed arrived at the following first-order singlet–triplet radiation less selection rules. Since

$$\langle S_{n,\pi^*} \mid \mathcal{H}_{so} \mid T_{n,\pi^*}\rangle \cong \langle S_{\pi,\pi^*} \mid \mathcal{H}_{so} \mid T_{\pi,\pi^*}\rangle \cong 0$$

and

$$\langle S_{n,\pi^*} \mid \mathcal{H}_{so} \mid T_{\pi,\pi^*}\rangle \neq 0$$

thus

$$n,\pi^* \leftrightarrow \pi,\pi^*, \quad n,\pi^* \not\leftrightarrow n,\pi^*, \quad \pi,\pi^* \not\leftrightarrow \pi,\pi^*$$

These selection rules are summarized in Figure 5. There is another factor of ~100 due to overlap considerations mentioned previously. Thus the nonfluorescence behavior as well as the strong phosphorescence properties of N-heterocyclics seem to result from a very efficient $S_1 \rightarrow T_1$ radiationless process. The values of Figure 5 are estimated from present qualitative observations and therefore should not be used for accurate calculations.

Fluorescence of (n,π*) character has been reported in only three N-heterocyclic compounds: *sym*-tetrazine (39a), dimethyl-*sym*-tetrazine (40), and 9,10-diazophenanthrene (231). All of these possess two adjacent ring nitrogen atoms. The interaction between the nonbonding orbitals on these two atoms is expected to be strong and, according to El-Sayed (76), should cause the energy of the lowest $^1(n,\pi^*)$ state to drop below that of the $^3(\pi,\pi^*)$ state. This would greatly reduce the rate of intersystem crossing from $^1(n,\pi^*)$, permitting fluorescence from this state to compete effectively with ISC as the principal mode of decay. An alternative explanation (72), which suggested that the lowest triplet state is higher in energy than the lowest singlet, has been shown by calculations (40, 193) to be incorrect.

These selection rules have also been used (76) to explain the greater ratio of phosphorescence to fluorescence in quinoline compared with its parent hydrocarbon, naphthalene. The presence of an (n,π*) triplet level between the lowest $^1(\pi,\pi^*)$ and $^3(\pi,\pi^*)$ levels in the former molecule leads to an enhancement of the intersystem-crossing process in quinoline.

Complete examination of carbonyl compounds has not as yet been carried out. However, the existing data suggest that they resemble N-heterocyclics in their behavior. Aromatic aldehydes and ketones, *e.g.*, benzophenone and benzaldehyde, show strong phosphorescence but no fluorescence. In these systems, the triplet state of the aromatic ring might lie between the n,π* singlet and triplet states of the carbonyl group. Aliphatic ketones and aldehydes, *e.g.*, formaldehyde, show both fluorescence and phosphorescence. In these systems, the absence of a low π,π* triplet state retards the intersystem-crossing process so that fluorescence competes successfully. In some of these systems, the total emission is weak, and the competition of other nonradiative processes (*e.g.*, photodissociation or photochemical reaction) might also be important.

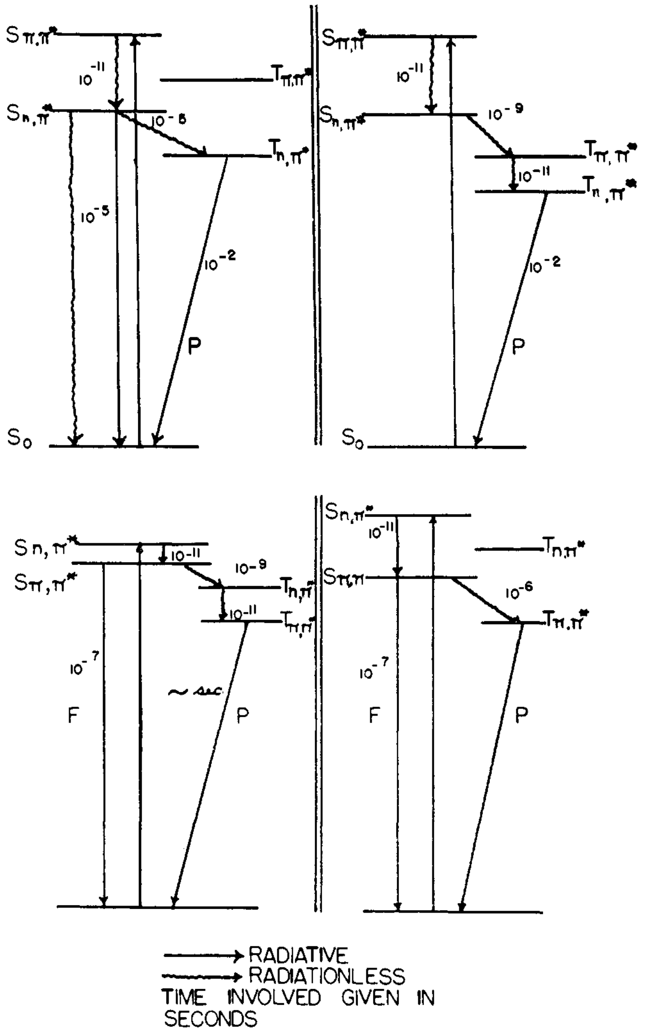


Figure 5.—Effect of the order and type of states on the rate of radiationless and emission processes in N-heterocyclic molecules.

Order-of-magnitude calculations have been carried out by Robinson and Frosch (326) on the rate of the different intersystem-crossing processes in benzene. Their results suggest that the intersystem-crossing process in this molecule follows the radiationless pathway

$$^1B_{2u} \rightsquigarrow {}^3E_{1u} \rightsquigarrow {}^3B_{1u}$$

Using time-resolved spectroscopic methods, Bhaumik and Nugent (22a) found that in Eu^+ chelates the radiationless relaxation between $^5D_1$ and $^5D_0$ is slower than that between $^5D_2$ and $^5D_0$. This difference was explained by showing that the expansion of the perturbation due to the ligand field in terms of spherical harmonics does not give terms of the correct symmetry to connect $^5D_0$ and $^5D_1$ but gives terms that might connect $^5D_0$ and $^5D_2$.

3. *Heavy-Atom Effects on S–T Radiationless Transitions*

The electronic integral of the probability for the T–S radiationless transition contains the spin–orbit matrix elements which are highly sensitive to the atomic number of the atoms in the vicinity of the excited electron. Increasing the atomic number is expected to increase the radiationless S–T transition probability. Introduction of a halogen in a compound or the presence of an iodide ion or other heavy atom or ion is known to quench the fluorescence emission and to increase the phosphorescence yield and probability, presumably due to an enhancement of the rate of the intersystem crossing and the $T_1 \rightarrow S_0$ radiative processes, respectively (see Table V).

McGlynn and co-workers (251) have examined the external heavy-atom effect (using alkyl halides in rigid glasses) on the intersystem-crossing process, and on the $T_1 \rightarrow S_0$ radiative and radiationless processes. They concluded that the $T_1 \rightarrow S_0$ radiationless process is less sensitive to heavy-atom perturbation than intersystem crossing, but more sensitive than phosphorescence. This conclusion is contradictory to the results obtained by Siegel and Judeikis (359), using combined esr and optical studies, which showed that the phosphorescence process is more sensitive to the heavy-atom than either the intersystem-crossing or the $T_1 \rightarrow S_0$ radiationless process. Experiments on the phosphorescence of charge-transfer complexes between aromatic hydrocarbons and tetrahalophthalic anhydride indicate (71) that the $T_1 \rightarrow S_0$ radiationless process is not greatly affected by the heavy atoms of the acceptor.

Robinson and Frosch (326) have shown how spin–orbit coupling might make a third-order contribution to the electronic integral for nonradiative multiplicity-forbidden transitions. In the case of a $T_1 \rightarrow S_0$ transition, for example, the T_1 state and the (vibronically degenerate) S_0 state of the solute cannot interact directly, but may be able to interact with solvent states, which are the ones that are strongly mixed by spin–orbit coupling, *i.e.*

$$\langle \mathrm{T}|\mathcal{H}'|\mathrm{S}\rangle = \frac{\langle \mathrm{T}|\mathcal{H}^{\mathrm{I}}|{}^3\psi^{\mathrm{b}}{}_{\mathrm{solv}}\rangle\langle {}^3\psi^{\mathrm{b}}{}_{\mathrm{solv}}|\mathcal{H}_{\mathrm{so}}|{}^1\psi^{\mathrm{a}}{}_{\mathrm{solv}}\rangle\langle {}^1\psi^{\mathrm{a}}{}_{\mathrm{solv}}|\mathcal{H}^{\mathrm{II}}|\mathrm{S}\rangle}{\Delta E_{\mathrm{b}}\Delta E_{\mathrm{a}}} \qquad \text{(Eq 10)}$$

In other words, the singlet state of the solute mixes electrostatically with the singlet state of the solvent (${}^1\psi^{\mathrm{a}}{}_{\mathrm{solv}}$), while the triplet state of the solute mixes with the triplet state of the solvent (${}^3\psi^{\mathrm{b}}{}_{\mathrm{solv}}$). Since the solvent contains a heavy atom, ${}^1\psi^{\mathrm{a}}{}_{\mathrm{solv}}$ and ${}^3\psi^{\mathrm{b}}{}_{\mathrm{solv}}$ are strongly mixed by spin–orbit interaction, *i.e.*, the transition from one to the other is not strongly forbidden by spin selection rules. The allowedness in turn (in third order) relaxes the spin forbiddeness of the solute S → T transition under consideration.

Because of the required violation of the (g,u) selection rule in the matrix elements and the larger energy denominators in benzene, Robinson and Frosch (326) believe that a smaller heavy-atom effect is expected for the $T_1 \leftrightarrow S_0$ radiationless transitions in this molecule. Of course in a mixture of heavy-atom and other solvents, it is expected that complexing would remove the center of symmetry. The role of vibrational overlap is expected to be the dominant cause for the lower sensitivity of the $T_1 \rightarrow S_0$ transition to external heavy-atom effects (compared to $S_1 \rightarrow T_1$ transition). The small effect on the $T_1 \rightarrow S_0$ process might lead to a larger observed heavy-atom effect on the $T_1 \rightarrow S_0$ radiative process that will tend to mask the effects on the $T_1 \rightarrow S_0$ radiationless process.

C. RADIATIONLESS PROCESSES IN RIGID MEDIA

1. *Observed Quantum Efficiencies and Rates*

In rigid solutions at low temperatures, diffusion-limited quenching processes are negligible, and photochemical reactions can ordinarily account for no more than a small fraction of the triplet-decay rates. Nevertheless, the absolute quantum yield measurements made by Gilmore, Gibson, and McClure (124) on a number of aromatic molecules in EPA showed that fluorescence and phosphorescence could rarely account for more than half of the decay of electronically excited molecules in this medium. It appears that radiationless transitions to the ground state compete with radiative emission, and that triplet states, with their long lifetimes, should be particularly subject to such generally rapid processes. This is in accord with the common observation that fluorescence quantum efficiencies are about

TABLE II

ABSOLUTE FLUORESCENCE AND PHOSPHORESCENCE QUANTUM YIELDS, OBSERVED AND CALCULATED (NATURAL) LIFETIMES

	Φ_P	Φ_F	τ_{obsd}, sec	τ_{nat}, sec
Benzophenone	0.84	0.0	0.006	0.008
	0.74^a	0.00^a	—	—
Acetone	0.04	0.26	0.0006	0.014
Benzene	0.26	0.26	7.0	21.0
	0.20^b	0.20^b	—	28
Chlorobenzene	0.04	0.0	0.004	0.007
Naphthalene	0.10	0.55	2.6	11.0
	0.03^a	0.29^b	—	—
Phenanthrene	0.135^a	0.12^a	—	—
Triphenylene	0.51	0.04	15.9	29.0

Data of Gilmore, Gibson, and McClure (124), except ^{a}from Ermolaev (94) and ^{b}Lim (225).

the same in vapor, liquid, and solid phases, while phosphorescence efficiencies and lifetimes are highly dependent on the environment. In most discussions, radiationless $S_1 \rightarrow S_0$ transitions are assumed to be of negligible importance, although there exists little rate data to support this assumption. The $S_1 \rightarrow S_0$ radiationless transition in azulene is probably an exception (160, 326). Lim (225) has estimated an upper limit of about $0.3k_F$ for the rate of the same transition in benzene, based on his quantum yield measurements and an assumed natural lifetime of 26 sec. Ermolaev's comparison of absolute fluorescence and phosphorescence quantum yields with "sensitized phosphorescence quantum yields" (94) does show that singlet quenching is not a highly important route of deactivation in rigid media, but the error associated with this type of experiment prevents demonstration of the complete absence of $S_1 \rightarrow S_0$ radiationless decay. Similarly, Lim and Laposa (226) find no evidence for a significant $S_1 \rightarrow S_0$ radiationless process in deuterated naphthalene and triphenylene.

Using emission lifetime and quantum efficiency data, Ermolaev (95) has calculated the radiationless decay rate constants (k_{PQ}) and natural lifetimes for the triplet states of a number of aromatic molecules (see Table III). The radiative and radiationless rates generally parallel each other, but it is notable that in every case the rate of radiationless decay exceeds that of emission, the difference being less in deuterated derivatives.

TABLE III

RADIATIVE AND RADIATIONLESS RATE CONSTANTS FOR TRIPLET → SINGLET TRANSITIONS IN RIGID GLASS SOLUTIONS (77°K) (DATA AND CALCULATIONS OF ERMOLAEV (96); THE PERCENTAGES OF DEUTERIUM SUBSTITUTION ARE NOTED IN BRACKETS[a])

Compound	Natural lifetime τ_0, sec	$k_P = 1/\tau_0$, sec^{-1}	k_{PQ}, sec^{-1}
Benzophenone	0.0062	160	50
Biphenyl-h_{10}	27	0.037	0.29
Biphenyl-d_{10} (85%)	27	0.037	0.25
Naphthalene-h_8	63	0.016	0.42
Naphthalene-d_8 (80%)[a]	63	0.016	0.03[a]
α-Chloronaphthalene	1.7	0.57	1.7
α-Bromonaphthalene	0.14	7.0	43
α-Iodonaphthalene	0.01	100	400
Quinoline	13	0.077	0.66

[a] Recent studies by other workers have found the phosphorescence lifetime ($1/k_T$) of naphthalene-d_8 to be 22 sec (37a, 195). Since $k_T = k_P + k_{PQ}$, this figure is clearly inconsistent with Ermolaev's value of 0.09 for k_{PQ}, which must have been measured in a sample of about 9-sec phosphorescence lifetime (suggesting that its deuterium content was considerably less than 80%). If Ermolaev's value of k_P is accepted, then k_{PQ} should be 0.03 sec^{-1}; this figure is given in the table in place of Ermolaev's value.

2. Environmental and Medium Effects

Gouterman (131) and Robinson and his co-workers (321, 326, 327) have pointed out the very important function of the solvent environment in radiationless decay; their theories were discussed in a preceding section of this review. It should suffice to mention here that Robinson (321) proposes that a kind of "tunneling" can provide a radiationless pathway between the zero level of the triplet state and high vibrational levels of the ground state. This process depends on the existence of a very small but finite overlap of vibrational eigenfunctions of the two states, and such overlap is favored by high-amplitude vibrational manifolds associated with the molecule itself and the system molecule-plus-environment. Intramolecular vibrations involving hydrogen atoms are predicted to be especially active in this respect, and the lower amplitude vibrations of the heavier deuterium atoms should, according to this hypothesis, prove less effective in facilitating radiationless decay. Thus Hutchison and Mangum (163) showed that the triplet lifetime of naphthalene–d_8 dissolved in deuteriodurene is 16.9 sec, while ordinary naphthalene decays in 2.1 sec in H- or D-durene. The influence of the environment was demonstrated in the methane and rare gas matrix experiments of Wright, Frosch, and Robinson (408), in which they measured phosphorescence lifetimes of benzene longer than any previously reported—16 sec in methane and argon at 4.2°K. Deuteriobenzene in the same two matrices gave 22 and 26 sec, respectively; thus these two media are almost as effective as deuteration in reducing the rate of radiationless decay. Kr and Xe matrices gave lifetimes of 1 and 0.07 sec, respectively, for both H- and D-benzene; the heavy-atom effect is presumed to be operative here.

These and other experiments led Robinson to conclude (321) that the phosphorescence lifetimes of deuterated molecules approach their true natural lifetimes, at least when the triplet state is not too low (*i.e.*, under conditions where the deuterium effect is expected to be sizable). The correctness of this assertion is highly doubtful, however; the results of Ermolaev (96) (see Table III) lead to natural lifetimes considerably in excess of the phosphorescence lifetimes of partly deuterated naphthalene and biphenyl. Radiationless triplet deactivation is shown to occur in both of these compounds, which unfortunately were not completely deuterium substituted. It does seem likely that the natural triplet lifetime of benzene is longer than 26 sec; theoretical calculations place it at several hundred seconds (141), and Craig, Hollas, and King (49) have estimated a value of at least 700 sec on the basis of their inability to detect S → T absorption in oxygen-free benzene.

Additional data illustrating the effects of deuteration on phosphorescence lifetimes have recently been provided by Kellogg and Schwenker (196), who examined a number of compounds dissolved in plastic films (see Table IV).

The effect of *viscosity* of the medium on the rate of radiationless T → S decay is still not entirely clear. The

TABLE IV

PHOSPHORESCENCE LIFETIMES OF NORMAL AND PERDEUTERATED HYDROCARBONS IN PLASTICS[a]

	298°K		77°K	
Compound	H	D	H	D
Naphthalene	1.5 sec	12.5 sec	2.4 sec	22 sec
Biphenyl	2.0	5.8	4.2	10.3
Phenanthrene	2.5	11.7	3.8	16.4
Triphenylene	9.4	12.2	16	23
Pyrene	0.4	2.5	0.5	3.2
Anthracene[b]	0.013	—	0.020	—

[a] Data of Kellogg and Schwenker (196), except where noted.
[b] Melhuish and Hardwick (255).

use of rigid media has long been considered a prerequisite for the observation of phosphorescence, the presumption being that collisions and other molecular motions that occur in fluids somehow act to enhance the decay process. Recent studies, however, indicate that this effect can largely be ascribed to bimolecular (pseudounimolecular) quenching of the triplet state by impurities, especially oxygen (see part IVA). A number of very careful experiments have succeeded in measuring decay rates in fluid solution that are comparable to values obtained for rigid media. One very important qualification must be made, however: namely, that most of these studies have been concerned with anthracene or other substances having relatively short triplet radiative lifetimes. If this work were extended to molecules having lifetimes greater by a factor of 10^3, say, any effect of viscosity on first-order decay should be correspondingly magnified, and a more complete answer to the question would be possible.

3. Temperature Effects on Triplet Decay

In their early studies of phosphorescence, Lewis, Lipkin, and Magel (221) found no significant effect of temperature (over a range of 20–296°K) on the triplet lifetime of fluorescein in boric acid glass. This result is at variance with the slight decrease in phosphorescence intensity and lifetime that is usually observed as the temperature is increased. Thus Pyatnitskii (307–311, 313) carried out a large number of studies on aromatic substances (mostly benzene derivatives) in the range 90–300°K, and found decay activation energies generally less than 500 cm^{-1}. In much of this and other early work the decay rates changed abruptly in different temperature ranges, casting doubts on the purity or uniformity of the samples.

The recent increased interest in radiationless transitions has led to more careful studies of the temperature dependence of triplet decay; the use of plastic media has facilitated this work, permitting investigations over wider temperature ranges. Melhuish and Hardwick (255) found the decay of triplet anthracene in polymethyl methacrylate to occur with negligible (~21 cm^{-1}) Arrhenius energy between 80 and 300°K. The normal and deuterated hydrocarbons studied by Kellogg and Schwenker (196) (Table IV) show non-uniform lifetime changes over the temperature range investigated; the lifetimes change most rapidly at the higher temperatures (just below 300°K), corresponding to activation energies of ~650 cm^{-1}. Near 77°K the activation energies are ~50 cm^{-1}.

Hadley, Rast, and Keller (137) have made a careful study of the phosphorescence decay of naphthalene and naphthalene-d_8 dissolved in durene crystal. They find activation energies of 3559 ± 79 and 3362 ± 35 cm^{-1}, respectively, for radiationless decay of the two triplets; no change in fluorescence intensity was noted over the temperature range 77–325°K, and no α-delayed fluorescence was detected. The authors suggest that these observed activation energies correspond to 2 quanta of a C–C skeletal vibration of naphthalene which is presumably involved in the $T_1 \rightarrow S_0$ radiationless process, but are unable to account for the high values (~10^{17} sec^{-1}) obtained for the radiationless rate constants in terms of the Franck–Condon factors that are expected to be involved. Olness and Sponer (271a) have measured the phosphorescence lifetime of naphthalene crystals at several temperatures in the range 4.5–15°K, but the inverse dependence on temperature is probably related to impurity effects.

4. Rate of Intersystem Crossing and Wavelength of Excitation

Multiplicity-forbidden character is known to reduce the probability of electronic transitions observed in absorption by a factor of ~10^{-6}; if intersystem crossing (ISC) is regarded as a spin-forbidden internal conversion process, then a value of $k_{IS} = 10^{13} \times 10^{-6} = 10^7$ sec^{-1} is predicted for the rate of ISC in aromatic hydrocarbon molecules (184). Absorption intensity measurements provide an estimate of 10^8 sec^{-1} for the fluorescence rate constant k_F, leading to a predicted ISC ratio

$$\chi = \frac{\Phi_T}{\Phi_F} = \frac{k_{IS}}{k_F} \cong 10^7/10^8 = 0.1$$

which is representative of the value experimentally observed in many aromatic molecules where radiationless processes are not especially rapid.

The rate constant k_{IS} seems to be a constitutive property of the molecule, and, in contrast with the nonradiative decay constant k_{PQ} (see next section), is relatively independent of state of aggregation, temperature, etc.

To whatever extent a simple two-dimensional potential energy diagram may have any meaning in a complex molecule, it might be assumed that, in general, S–T "crossing" might occur at some point *above* the zero-point levels of the respective curves. Kasha and Powell (190) pointed out that an accurate comparison of the activation energy of α-delayed fluorescence with the difference between the zero levels of fluorescence and phosphorescence should give some indication of the location of this crossing point, but the studies carried out on dyes (whose spectra are very broad) do not provide any definitive information (5, 221). Very recently, however, Stockburger (380) has found virtually identical values for these two quantities in his study of benzaldehyde vapor phosphorescence. Actually, there seems to be little point in bringing in the concept of potential energy crossing, since classical crossing is not required for rapid radiationless transitions to occur if vibrational overlaps and tunneling are considered (326).

It is generally *assumed* that internal conversion is so rapid that ISC always proceeds from the lowest singlet excited state, and therefore the phosphorescence yield and k_{IS} should be independent of the initial level of excitation, providing that it is not so high that bond dissociation or ionization can occur. In molecules, where internal conversion is not very fast, one might expect the phosphorescence-to-fluorescence ratio to increase (but never to decrease) as the energy of excitation is increased (326). Ferguson (108) found the phosphorescence yields of the F, Cl, and Br monohalonaphthalenes to be unchanged throughout excitation wavelengths corresponding to the first two electronic transitions of these molecules. O'Dwyer, El-Bayoumi, and Strickler (269), on the other hand, reported an increase in the phosphorescence/fluorescence ratios of chrysene and hexahelicene when excited in their higher singlet absorption bands. Recent studies by Wessel and El-Sayed (403a) showed that this effect is not reproduced in the case of chrysene. There appears to be complications due to the low solubility of the compound (M. O'Dwyer and J. Laposa, private communications). The effect on hexahelicene has not as yet been reexamined. Bauer and Bączyński (17) found that the phosphorescence/fluorescence ratio for fluorescein in boric acid glass increases with energy of the exciting light, and then falls off again at still higher levels of excitation; this behavior may be connected with the photochemical activity of their medium or impurity effects. Mokeeva and Sveshnikov (259), measuring emission lifetimes and phosphorescence intensities of several dyes at two temperatures, conclude that k_{IS} is greater if higher vibronic levels of S_1 are (thermally) populated, but their report is difficult to interpret and the results are open to other explanations.

Zelinskii and Kolobkov (414) have attempted to relate the energy of the S_1 state to the ISC ratio in several substituted phthalimides, whose fluorescence maxima are quite subject to solvent effects. Using 37 different solvents, they plotted ISC ratio as a function of fluorescence wavelength maxima (ranging from 17 to 27 kK), and found the points for each phthalimide to cluster about different curves, suggesting a strong apparent dependence of the type they propose.

III. RADIATIVE PROCESSES INVOLVING THE LOWEST TRIPLET STATE

A. THEORY

1. *Spin–Orbit Hamiltonian and S–T Mixing*

In the approximation that neglects the parts of the Hamiltonian representing spin–orbit interaction, one can speak of having pure singlet and pure triplet states. The singlet state is represented by an antisymmetric wavefunction which is a product of a symmetric space part and antisymmetric spin function $(1/\sqrt{2})(\alpha\beta - \beta\alpha)$. The triplet wavefunctions are antisymmetric functions composed of an antisymmetric space function multiplied by the three symmetric spin functions $\alpha\alpha$, $\beta\beta$, $(1/\sqrt{2})(\alpha\beta + \beta\alpha)$. If the singlet and triplet states both have the same configuration, the difference in the sign (*plus* in the singlet but *minus* in the triplet state) of the linear combination of the space part of the two one-electron functions gives rise to a value for the energy of the triplet state which is lower than that for the singlet state (Hund's rule). Since most stable molecules have singlet ground states (all electrons are paired), *the lowest excited level must then be a triplet state.*

In actuality the singlet and triplet states are never pure, even in helium. Spin–orbit interaction, which is highly sensitive to the Coulombic nuclear field, mixes the two types of states. Physically this interaction can be visualized in the following manner. In the singlet state the two electrons have opposite spins whereas in the triplet state they have parallel spins. One can change a singlet state into a triplet state (or *vice versa*) by the application of a force tending to change the direction of spin magnetic moment of one of the electrons.

In an atomic or molecular system the magnetic moment $\vec{\mu}$ of a spinning electron is related to its angular momentum $\vec{s}$ by the following expression.

$$\vec{\mu} = -\,[|e|/mc]\vec{s} \qquad \text{(Eq 11)}$$

The interaction energy between the magnetic dipole moment $\vec{\mu}$ of an electron and the magnetic field due to its orbital motion with velocity $\vec{v}$ in the electric field of the nucleus $\vec{E}$ is classically given by

$$\mathcal{H}_1 = -\,\vec{\mu}\cdot(\vec{E} \times \vec{v}) \qquad \text{(Eq 12)}$$

Substituting Eq 11 in Eq 12 and taking into account relativistic effects, the main part of the spin–orbit Hamiltonian results

$$\mathcal{H}_1 = +\frac{|e|}{2mc^2}(\vec{E} \times \vec{v})\cdot\vec{s} = +\frac{|e|}{2m^2c^2}(\vec{E} \times \vec{p})\cdot\vec{s} = \frac{1}{2m^2c^2}(\text{grad}\,\vec{V} \times \vec{p})\cdot\vec{s} \qquad \text{(Eq 13)}$$

where V is the potential energy of the electron. For an atomic Coulomb field $V = -ze^2/r$, and Eq 13 becomes

$$\mathcal{H}_1 = \frac{ze^2}{2m^2c^2}\,\frac{1}{r^3}\,(\vec{r} \times \vec{p})\cdot\bar{s} = \frac{ze^2}{2m^2c^2}\,\frac{1}{r^3}\,\vec{L}\cdot\vec{S} \quad \text{(Eq 14)}$$

For general central fields for many electrons where $V = V_{(r)}$

$$\mathcal{H}_1 = \frac{1}{2m^2c^2}\sum_{i}\frac{1}{r_i}\,\frac{\partial V_{(r_i)}}{\partial r_i}\,\vec{L}_i\cdot\vec{S}_i = \sum_{i}\zeta_{(r_i)}L_i\cdot\vec{S}_i \quad \text{(Eq 15)}$$

where the sum is over all electrons and the spin–other orbit interaction (*i.e.*, the interaction between the spin of one electron and the spin of the other) is being neglected.

The above expressions do not contain all terms of the total spin–orbit Hamiltonian $\mathcal{H}_{so}$. In the absence of an external field, the full form of the latter is given by (204)

$$\mathcal{H}_{so} = \alpha^2\Bigg[\sum_{\mu}\sum_{i}\frac{z_\mu}{r_{i\mu}{}^3}L_i\cdot\vec{S}_i - \sum_{i,j}\frac{\vec{P}_i \times \vec{r}_{ij}}{r_{ij}{}^3}\cdot\vec{S}_i + 2\sum_{i,j}\frac{\vec{P}_j \times \vec{r}_{ij}}{r_{ij}{}^3}\cdot\vec{S}_i\Bigg] \quad \text{(Eq 16)}$$

where α is the fine structure constant ($= {}^1/_{137}$ if L, S, z, and r are in atomic units), P is the linear momentum operator, and z_μ is the effective nuclear charge of the μth nucleus.

The first term in the bracket is that derived previously (Eq 13); it represents the coupling between the spin and orbital momentum of an electron, through interaction with the attractive nuclear field of z_μ. The second term represents the coupling of the spin and orbital motions of one electron i with the repulsive field of another electron j. The third term represents the coupling of the spin angular momentum of an electron i with the orbital angular momentum of another electron j through the repulsive electrostatic force they exert upon one another. The last term represents the spin–other orbit interaction and is normally very small. The second term is found (126a) to be comparable to the first one in helium in which z_μ is small and the two electrons are relatively close to one another. As z and the principal quantum number of the excited electrons increase, the relative importance of the first term increases.

The expectation value of the spin–orbit interaction energy can, in principle, be calculated using the above Hamiltonian and approximate wavefunctions. If the first term of $\mathcal{H}_{so}$ is used

$$\langle {}^1\Psi\,|\mathcal{H}_{so}|\,{}^3\Psi\rangle = \langle {}^1(\Psi\gamma)\,|\mathcal{H}_{so}|\,{}^3(\Psi\gamma)\rangle = \alpha^2\sum_{\mu}\sum_{i}\left\langle \frac{z_\mu}{r^3}\,{}^1\Psi\,|L_i|\,{}^3\Psi\right\rangle\cdot \left\langle \frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)|\vec{S}|\begin{pmatrix}\alpha\alpha\\ \beta\beta\\ \frac{1}{\sqrt{2}}(\alpha\beta + \beta\alpha\end{pmatrix}\right\rangle \quad \text{(Eq 17)}$$

where Ψ and γ are the space and spin zero-order functions, respectively. Integration over the spin coordinates can be carried out, and one can usually find that one of the components of S gives a nonvanishing value. In order for the space part not to vanish, the direct product of the irreducible representations of ${}^1\Psi$ and ${}^3\Psi$ must contain the irreducible representation to which one or more of the components of L, L_x, L_y, and L_z belongs. The latter transform like rotation operators R_x, R_y, and R_z, respectively, in the point group of the molecule. These are the main selection rules for spin–orbit coupling (240a, 401a). In order to obtain the magnitude of the interaction, the actual integration of the space part of Eq 17 has to be carried out. For polyatomic molecules this has been done for only a few cases.

2. S–T Mixing and Phosphorescence

Because of the spin–orbit interaction, the singlet states of a polyatomic molecule have a certain amount of triplet character and the lowest triplet state similarly has some singlet character. According to the first-order perturbation theory, the total wavefunction ${}^3\Psi_1$ (which is the zero-order wavefunction perturbed by the spin–orbit interaction) is then written as

$${}^3\Psi_1 = {}^3\Psi_1{}^\circ + \sum_{k}\delta_{1k}{}^1\Psi_k{}^\circ \quad \text{(Eq 18)}$$

where the summation is carried over the singlet manifold and δ_{1k} is the mixing coefficient between ${}^3\Psi^\circ$ and ${}^1\Psi_k{}^\circ$. According to perturbation theory, δ_{1k} is given by

$$\delta_{1k} = \frac{\langle {}^3\Psi_1{}^\circ|\mathcal{H}_{so}|{}^1\Psi_k{}^\circ}{|{}^3E_1 - {}^1E_k|} \quad \text{(Eq 19)}$$

The ground-state wavefunction is given by

$${}^1\Psi_0 = {}^1\Psi_0{}^\circ + \sum_{j}\delta_{0j}{}^3\Psi_j{}^\circ \quad \text{(Eq 20)}$$

and the summation is carried over all states of the triplet manifold.

The radiative transition probability between ${}^3\Psi_1$ and the ground state is proportional to the square of the transition moment integral, $\vec{M}_{T_1,S_0}$, given by

$$\vec{M}_{T_1S_0} = \langle {}^3\Psi_1|\sum_{i} e\vec{r}_i|{}^1\Psi_0\rangle = \sum_{k}\delta_{1k}\bar{M}_{S_k,S_0} + \sum_{j}\delta_{0j}\vec{M}_{T_j,T_1} \quad \text{(Eq 21)}$$

where the summation is carried out over all the electrons i. Terms like $\vec{M}_{T_1{}^\circ,S_0{}^\circ}$ and $\vec{M}_{T_j{}^\circ,S_i{}^\circ}$ vanish because of spin orthogonality (spin selection rules).

Equation 21 gives rise to the following important conclusion: the phosphorescence is an emission having an energy equal to the difference in energy between the ground state and the lowest triplet state, but with polarization characteristics identical with those of the perturbing transitions $S_k \leftrightarrow S_0$ and $T_j \leftrightarrow T_1$.

3. *Vibronic Perturbations*

The Hamiltonian used in the previous section is completely electronic in nature; the nuclear coordinates are held fixed in space. In some cases, such perturbation vanishes because of molecular or local symmetry considerations. In these cases when nontotally symmetric vibrations slightly distort the molecule, exact cancellation of terms is avoided and vibronic terms can introduce singlet–triplet mixing.

Vibronic interaction can appear either as a first- or second-order perturbation. The total Hamiltonian can be written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{so} \qquad \text{(Eq 22)}$$

where $\mathcal{H}_0$ contains the usual kinetic and potential energies for the electrons as well as the pure spin-energy operators. Both $\mathcal{H}_0$ and $\mathcal{H}_{so}$ contain nuclear coordinates as parameters.

The Hamiltonian given in Eq 8 can be expanded in a Taylor series in normal coordinates of the ground electronic state for $S_0 \rightarrow T_1$ absorption or of the emitting triplet state for $T_1 \rightarrow S_0$ emission. The following terms are obtained (3) to first order in the nuclear displacement

$$\mathcal{H} = \mathcal{H}^\circ + \sum_a \left(\frac{\partial \mathcal{H}}{\partial Q_a}\right)_0 Q_a = \mathcal{H}_0{}^\circ + \mathcal{H}_{so}{}^\circ + \sum_a \left(\frac{\partial \mathcal{H}_0}{\partial Q_a}\right)_0 Q_a + \sum_a \left(\frac{\partial \mathcal{H}_{so}}{\partial Q_a}\right)_0 Q_a = \mathcal{H}_0 + \mathcal{H}_1 + \mathcal{H}_2 + \mathcal{H}_3 \qquad \text{(Eq 23)}$$

where the superscript zero in the leading term refers to the equilibrium nuclear position (at which the partial derivatives are evaluated); Q_a refers to the $3N - 6$ normal coordinates of the appropriate electronic state.

The second ($\mathcal{H}_1$), third ($\mathcal{H}_2$), and fourth ($\mathcal{H}_3$) terms can mix singlet and triplet states. $\mathcal{H}_1$ and $\mathcal{H}_3$ mix the two types of states by first-order perturbation, but $\mathcal{H}_2$ requires second-order perturbation (spin orbit $\mathcal{H}_1$–vibronic $\mathcal{H}_2$).

Equation 9 gives rise to important types of selection rules.

1. Because of the nature of the expansion indicated above, perturbing vibrations must possess the right symmetry in the point group to which the originating state belongs. In emission, the geometry of the molecule in the triplet state determines vibronic selection rules whereas in absorption, the geometry of the ground electronic state determines vibronic selection rules.

2. Both $\mathcal{H}_2$ and $\mathcal{H}_3$, are energy expressions, invariant to symmetry operations, *i.e.*, totally symmetric to all operations. Therefore, $(\partial\mathcal{H}_0/\partial Q_a)_0$ in $\mathcal{H}_2$ and $(\partial\mathcal{H}_{so}/\partial Q_a)_0$ in $\mathcal{H}_3$ should have the symmetry properties in electronic coordinates identical with that of Q_a (the perturbing vibration) in nuclear coordinates. The direct product of the irreducible representation of the two states to be mixed by $\mathcal{H}_2$ or $\mathcal{H}_3$ must then be identical with or include the irreducible representation of the perturbing vibration Q_a.

The relative magnitudes of these perturbations for molecules containing H, C, or N are $\mathcal{H}_1 \sim 1$, $\mathcal{H}_2 \sim 500$, and $\mathcal{H}_3 \sim 0.01$ cm^{-1}. In spin–orbit perturbation, $\mathcal{H}_2$ enters in second order and, therefore, becomes a less important perturbation than $\mathcal{H}_1$ (if $\mathcal{H}_1$ is nonvanishing). For molecules with heavy atoms both $\mathcal{H}_1$ and $\mathcal{H}_3$ are expected to increase in importance ($\mathcal{H}_2$ increases in second order).

4. *Theoretical Predictions of Phosphorescence Mechanisms*

Since the last review (189) on the subject of phosphorescence, one of the most important contributions to the field has been the careful examination of the mechanism by which the lowest triplet state of aromatic molecules acquires its radiative properties. Both theoretical and spectroscopic methods have been applied and an understanding of the gross aspects of the emission process has been acquired.

McClure (240) proposed to explain the observed decay time of aromatic hydrocarbons by assuming that the spin–orbit interaction energy is the sum of the spin–orbit energies of the atoms. This simple picture gave values for the lifetime which were much smaller than those observed for aromatic hydrocarbons. Further work by McClure (242) led to a more accurate method of describing the spin–orbit interaction in benzene. The long phosphorescence lifetimes characteristic of aromatic compounds were found to be due to the vanishing contribution of the one- and two-center terms resulting from the spin–orbit interaction between S_{π,π^*} and T_{π,π^*} states that is possible in *planar* molecules. A calculation of the spin–orbit energy between π,π^* states was later carried out for benzene by Hameka and Oosterhoff (141). Assuming that $^3B_{1u}$ is the emitting triplet state, mixing with the $^1E_{1u}$ state is found to give the best agreement with experiment. The predicted lifetime is found to be 190 sec. Previously, it was found that mixing the lowest triplet level with a state of the σ,π^* type leads to a predicted radiative lifetime of several hundred seconds (258). Observed radiative lifetimes determined by different methods give different values; even using the same method, different workers report different values. For naphthalene the values of 14 and 63 sec are obtained from quantum yield measurements by McClure (124) and Ermolaev (94), respectively. A value of 17 sec is suggested by Robinson (321) on the assumption that the rate of the radiationless process in the perdeuterated compound is very slow in comparison with radiative decay. In this case the observed lifetime of 17 sec for the $C_{10}D_8$ phosphorescence is assumed to correspond to its radiative lifetime. According to this proposal, the radiative lifetime of benzene should be 26 sec. The absorption studies of Craig and co-workers (49) on thoroughly degassed liquid benzene indicate a radiative lifetime longer than 700 sec! This result, which agrees with the values theoretically predicted, indicates that the observed emission lifetime is probably not the radiative one. Some recent studies on the quantum yield of the phosphorescence of deuterated naphthalene give a value of $\sim$0.3 (94, 195). The absorption studies require a yield that is at least an order of magnitude less than 0.3. If both the quantum yield and absorption measurements are correct, the discrepancy between the emission and absorption results and those between the emission and theoretical predictions can be interpreted to mean that the $T_1 \leftrightarrow S_0$ transition in rigid medium is ten times more allowed than in fluid solution; *i.e.*, the *rigid medium* (not temperature) enhances the $T_1 \leftarrow S_0$ radiative transition! This is certainly an unexpected result and therefore the important question concerning the actual natural (radiative) lifetime of the phosphorescence emission of aromatics should be considered unsolved.

Theoretical predictions are in good agreement with observed lifetimes for n,π^* $S \leftrightarrow T$ radiative transitions. Sidman showed (356) that in formaldehyde, spin-orbit induced mixing between the $^3A_2$ (n,π^*) and $^1A_1$ (π,π^*) states leads to a triplet lifetime similar to that observed in phosphorescence. Calculations by Clementi and Kasha (45) and by Sidman (357) were equally accurate in predicting the radiative lifetime of pyrazine phosphorescence. The radiative lifetimes of $^3(\pi,\pi^*)$ states are at least 100 times greater than for $^3(n,\pi^*)$ states, for the reasons discussed in part II.

B. EXPERIMENTAL STUDIES

1. *Experimental Observation of Phosphorescence*

The phenomenon of phosphorescence is the most familiar manifestation of the triplet state, and a vast quantity of literature now exists on this topic. The most extensive experimental survey of phosphorescent substances is still that of Lewis and Kasha (218), who photographed the emissions of 89 compounds. Clar and Zander (43) presented the phosphorescence spectra of a number of aromatic hydrocarbons, and lifetime measurements on a large variety of compounds have been made by Dikun, Petrov, and Sveshnikov (65a) and McClure (240).

Aromatic hydrocarbons have received the most attention in phosphorescence studies, due both to their relatively long (0.1–10 sec) observed lifetimes and to the large body of knowledge, both theoretical and empirical, that we now have of their structures and properties. Most aromatic compounds phosphoresce, and some of the more symmetrical ones have very long lifetimes; however, as the energy of the lowest triplet level approaches that of the ground state, nonradiative decay processes become more likely (321, 327) and phosphorescence is weakened. Thus phosphorescence has not been observed in tetracene (in which the triplet has been located by $S \rightarrow T$ absorption at 10,250 cm^{-1} (250)), pentacene, or azulene (326). In some compounds, the lack of detectable phosphorescence is due to constitutive effects that are not entirely understood; ethylene, *trans*- (but not *cis*-) stilbene, perylene, and pyridine are examples. The effect of substituents on triplet lifetimes and intensities is usually minor (65a, 311) when heavy atoms are not involved, although certain substituents ($-NO_2$, for example,) definitely tend to repress phosphorescence.

In order to observe phosphorescence, it must be possible to populate the triplet state at a rate that is greater than that of all nonradiative triplet relaxation processes; in addition, the total radiationless decay rate must not exceed the phosphorescence rate by a large amount. The nature of the individual molecule imposes a lower limit on the radiationless decay rate, but it is well known that concentration and environment strongly influence radiationless relaxation processes (see the discussion elsewhere in this article), and these factors must be adjusted to maximize the radiative phosphorescence yields.

Most phosphorescence studies have been conducted in (supercooled) rigid glass solutions. By far the most popular mixture is "EPA," which consists of ether, isopentane, and absolutely dry ethanol (but preferably not commercial *absolute* alcohol, which contains benzene) in 5:5:2 volume ratio. Ether–ethanol, methylcyclohexane, and glycerol are also frequently used. A list of 60 such rigid-glass solvents has been given by Smith, Smith, and McGlynn (369). EPA is not always completely inert; the spectra of heterocyclic compounds in this medium have been altered by hydrogen bonding between the ethanol and nonbonding heteroatoms (344), and evidence of photoreactions with hydrocarbons at high light intensities has been reported (50, 105). Anomalous behavior can result if solute concentrations are too high; von Foerster (112) found that phosphorescence lifetimes of naphthalene and phenanthrene in EPA decreased slightly when concentrations were increased from 0.005 to 0.1 *M;* at the same time, a new, short-lived phosphorescence appeared, probably coming from solute microcrystals. The unsuspected presence of microcrystals has led to a number of incorrect interpretations of spectra. Schmillen and Tschampa (338) have shown that the microscopic structure of supercooled ethanol solutions (and its change with temperature) can strongly alter the intensity and lifetime of phosphorescence spectra.

Boric acid and sugar glasses have been used as media for phosphorescence studies since "classical" times, but are highly unsatisfactory for most modern work and their use is to be strongly discouraged. High temperatures are required to prepare these glasses, and the concomitant decomposition of the solute may be a serious problem, or at least an uncertainty. Each medium suffers from further disadvantages: glucose glasses (274) are very sensitive to moisture and subject to contamination by oxidation products which are presumably formed during preparation of the glass (273). Boric acid glass acts as a strong acid (36) that can promote photoionization of dissolved hydrocarbons (36, 174), many of which have excited states of basic character (57). Lewis, Lipkin, and Magel (221) found phosphorescence lifetimes to vary with the method of preparation of boric acid glasses. In addition, boric acid usually contains trace impurities that interfere with absorption in the ultraviolet region (272). Nevertheless, many workers continue to use this medium, even with dyes that are expected to be even more sensitive to decomposition and photoreactions than hydrocarbons.

Oster and his co-workers (273) have explored the use of plastics as rigid media in phosphorescence studies. They have introduced aromatic hydrocarbons into polycarbonates, acrylics, polystyrene, and cellulose polymers. Polyvinyl acetate is a useful medium for water-soluble dyes. Oster, Geacintov, and Cassen (272) have shown how differences in oxygen diffusion rates, local viscosities, and specific interactions with different polymer matrices can influence the intensity, lifetime, and shape of phosphorescence spectra, using 1,2,5,6-dibenzanthracene as an example. Czarnecki and Kryszewski (53) have monitored the diffusion of oxygen and hydrogen (which displaces the oxygen) into naphthalene-containing polymer films by observing the sharp boundary of phosphorescence between quenched and nonquenched regions. Plastic media have been employed in recent studies of hydrocarbon triplet decay (196, 255), phosphorescence polarization studies (77, 78), emission efficiencies (195), and intermolecular energy transfer (18, 19, 194). Plastics will undoubtedly become much more widely used in the future, especially in temperature-dependence studies; it is important to remember, however, that the microscopic structure of these materials is complex and subject to non-uniform changes with temperature. The presence of luminescent impurities (and unreacted monomer (16)) in commercial polymeric materials as well as the ultraviolet absorption of the plastic itself will very likely prove to be a serious limitation in emission studies.

The use of frozen aliphatic hydrocarbon media in both absorption and emission studies was pioneered by Shpol'skii (349) (see ref 347 for a review). The snowlike polycrystalline solids yield sharp "quasi-linear" spectra in which normally broad molecular vibronic peaks are narrowed down to only a few cm^{-1}, permitting high-resolution studies of large molecules in condensed phase. The degree to which the fine structure is resolved is highly sensitive to the relative sizes of the solute molecule and solvent crystal lattice (346). There is usually a splitting of the spectrum into as many as five "multiplets" separated by <100 cm^{-1}, each of which is thought to correspond to emission from sets of molecules situated in different local environments (351). The origin of the extremely narrow "phononless" spectrum has been attributed to a mechanism akin to that responsible for the Mössbauer effect (315).

The Shpol'skii method has found wide use in the Soviet Union (347), and by Kanda and co-workers in Japan. Frozen solutions of CCl_4 and dioxane have been employed by Kanda and Shimada, who have shown that benzene is apparently deformed to a lower symmetry in these media (177).

Phosphorescence studies on substitutional solid-solution mixed crystals and on single "pure" crystals are discussed in section IV of this review.

The importance of *extreme purity* in phosphorescence studies cannot be too strongly emphasized. The purity of commercial hydrocarbons, which are mostly nothing more than refined coal tar, is often quite difficult to assess, particularly in regard to isomeric substances having similar emission spectra. Zone-refining can reduce but frequently cannot remove certain impurities (for example, anthracene from phenanthrene, *p*-terphenyl, or fluorene), and it may create new ones through thermal decomposition. It is doubtful that the true emission spectrum of some hydrocarbons (*e.g.*, chrysene) has ever been observed; recourse to synthetic compounds will ultimately be necessary to settle the matter.

Failure to recognize the presence or effects of impurities has led to much confusion in the literature, particularly in the Soviet Union, where the nonexponential phosphorescence decay observed in phenanthrene and other compounds (33, 198, 384) led to the development and rather wide acceptance of a theory that these substances possess "multiple metastable levels" (5, 234, 290) (*i.e.*, in addition to the one ordinary triplet state) which emit at different rates and wavelengths. Teplyakov (390) has since shown that 30–35 passes of zone-refining is sufficient to eliminate these effects from the solution spectrum of phenanthrene. A similar nonexponential decay of acriflavine phosphorescence observed by Kato and Koizumi (183) has been attributed to inhomogeneities in the rigid medium (329).

Benz and Wolf (20) have shown the extent to which anthracene-impurity fluorescence dominates that of phenanthrene in crystals of highly zone-refined material. Since triplet energy transfer is generally even more efficient than singlet transfer, workers under-taking phosphorescence studies on crystals should exercise the utmost care regarding purity; the remarks of Sternlicht, Nieman, and Robinson (376) and Olness and Sponer (271a) on the phosphorescence of "pure" hydrocarbon crystals are of interest in this connection.

2. Radiative Properties of Heterocyclic Compounds

a. N-Heterocyclic Molecules

The introduction of a heteroatom into an aromatic ring system confers additional spectroscopic properties upon a molecule, since there now exists the opportunity for excitation of nonbonding electrons (associated with the heteroatom sp^2 orbital) into the π system (184); the spectroscopy of such molecules (mainly the azines) has been discussed extensively by Kasha (184, 187, 188), Goodman (126), Sidman (356), and Murrell (263).

From the standpoint of the triplet state, there are two important factors to consider in heteromolecules. First, triplet states can be of (n,π^*) or (π,π^*) character, and molecules can be classified according to which of the two triplet levels is lower. The effect on the rate of radiationless processes of having these two different types of states has been discussed earlier. The (n,π^*) triplet state has stronger radiative power than a π,π^* triplet state. The lifetime of a $\pi^* \rightarrow n$, $T_1 \rightarrow S_0$ emission is $\sim 10^{-2}$ sec whereas that of a $\pi^* \rightarrow \pi$ emission is >10 sec. This difference is due to the following.

1. The spin–orbit perturbation of an n,π^* triplet level involves π,π^* transitions, which are strongly radiative and give rise to nonvanishing one-center spin–orbit terms on the nitrogen (45, 357).
2. The spin–orbit perturbation of a π,π^* level is thought to involve both the n,π^* and σ,π^* transitions, neither of which is strongly radiative.

Except for pyridine, the monocyclic azines are believed to have lowest triplet states of (n,π^*) character. Of these, *pyrazine* (1,4-diazine) has been the most thoroughly studied; Goodman and Kasha (128) assigned the phosphorescence to $^3B_{3u}\ (n,\pi^*) \rightarrow {}^1A_g$; the quantum yield is very high and the lifetime is 0.02 sec. Shimada (344) has reexamined the phosphorescence spectrum, using a large variety of media at 90°K; his vibrational analysis differs slightly from that of Goodman and Kasha. The sharpest spectra were obtained in matrices of cyclohexane, CCl_4, dioxane, and benzene; in the latter, the pyrazine (normally D_{2h}) is apparently deformed slightly to a C_{2v} configuration. Shimada further established the (n,π^*) character of the phosphorescence by demonstrating its disappearance in acid media, as well as its partial disappearance in the monoprotonated form, in which the phosphorescence is red-shifted by 370 cm^{-1}. These results should not be reproduced by Krishna and Goodman (206, footnote).

El-Sayed and Robinson (85) pointed out that the two heteroatoms in diazines should give rise to two $n \rightarrow \pi^*$ transitions, one allowed and the other forbidden. Although formally degenerate, intramolecular electronic interactions can split the two states; crude calculations indicate an upper limit of 24 cm^{-1} for this splitting. These authors also showed that the S–T absorption and phosphorescence involve the same electronic state $(^3B_{3u})$; this state must therefore be *lower* than its nearly degenerate partner, which is assigned to $^3B_{2g}$. This also is in accord with their calculations, which place the B_{3u} and B_{2g} states in reverse order of that found in the singlet manifold.

The phosphorescence of *pyrimidine* (1,3-diazabenzene) has been studied by Krishna and Goodman (206) and by Shimada (345), who assigned the emitting triplet to $^3B_2\ (n,\pi^*)$ on the basis of vibrational analysis and solvent effects. *Pyridazine* (1,2-diazabenzene) does not emit even in rare gas matrices at 4°K (74). Theoretical arguments (127, 254) place the lowest $^1(n,\pi^*)$ state below the lowest π,π^* in pyridazine, but above it in pyrazine and pyrimidine. El-Sayed (74) suggests that the absence of phosphorescence in pyridazine may reflect the much lower probability expected for $^1(n,\pi) \rightarrow {}^3(n,\pi^*)$ intersystem crossing as compared to the $^1(n,\pi^*) \rightarrow {}^3(\pi,\pi^*)$ process (that might take place in pyrazine and in pyrimidine). Since fluorescence is not observed, it is suggested that radiationless processes from the singlet state of pyridazine might be important. There are spectroscopic results indicating that these processes occur in the singlet state of quinoline (76, 150). Certainly, enhanced radiationless transitions from the lowest singlet or triplet state might be expected of highly polar molecules like pyridazine and pyridine on the basis of vibrational overlap factors (75) as well as strong coupling with the environment. These factors might explain the nonradiative property of pyridine.

The polycyclic azines studied so far all appear to have (π,π^*) lowest-triplet states; Müller and Dörr (261) showed that absorption in the $^1(n,\pi^*)$ bands of seven azanaphthalenes (quinoline, etc.) gives a phosphorescence very similar to that of naphthalene itself, and polarization studies (discussed elsewhere) have confirmed this triplet assignment in these and many other polycyclic azines (66, 82, 136). El-Sayed and Kasha (73) and Ermolaev and Svitashev (91) have found that quinoline in hydroxylic glasses shows both fluorescence and phosphorescence but in hydrocarbon glasses shows only phosphorescence. This difference in emission behavior is due to the fact that in the former glass the lowest excited singlet state is of the π,π^* type whereas in the latter glass it is of the n,π^* type. Heckman (142) found that the phosphorescence of carbazole, dibenzofuran, and dibenzothiophene is very similar to that of fluorene and is thus of (π,π^*) character.

b. Other Molecules Containing Heteroatoms

Compounds containing carbonyl, nitro, diazo, thio, and similar groups generally have (n,π^*)-emitting triplet states (187, 263). Acetone and other aliphatic ketones have phosphorescence lifetimes of around 0.001 sec (240). *Formaldehyde* has probably received the most study of any ketone (34, 46, 320) (see the review by Robinson and DiGiorgio (325). As in other ketones, the assignment of the triplet state is ^{3}U (symmetry-forbidden transition to ground state) in Platt's notation (292).

Glyoxal ($(CHO)_2$) phosphoresces in the 5200-A region; the emission origin corresponds to a band of the ^1A_u system, and this prevented its identification and assignment until Brand's (29) study of D_2-glyoxal, in which the 0,0-band is red-shifted by 155 cm^{-1}. *Biacetyl* (2,3-butanedione) has been studied very extensively (270) and is of great photochemical interest; absorption of light of wavelength less than 4000 A can lead to photodecomposition. Biacetyl is unusual in that its yellow-green phosphorescence is visible in vapor and liquid phase as well as in solid media. The origin of the $^3A_u \leftrightarrow {}^1A_g$ transition occurs at 19,197 cm^{-1} in the vapor (22), but Sidman and McClure (354) reported a gap of ~500 cm between the origins of the S–T absorption and the phosphorescence in experiments on the crystal and rigid glass solutions at 20°K. The two origins are assigned to two triplet states, ^3A_u (20,421 cm^{-1}) and ^3B_g (20,355 cm^{-1}), defined by absorption and emission origins, respectively. Another green emission (this one very weak) may also originate at 20,355 cm^{-1}; it has not yet been explained, but might be crystal-induced. No splitting of the n,π* levels of diketones has been observed; glyoxal and biacetyl both have *trans* configurations, making the necessary interaction unlikely, while the *cis*-diketones have not been examined under conditions that would permit resolution of small splittings (263).

Benzaldehyde, acetophenone, and benzophenone have recently been studied in both absorption and emission by Kanda, Kaseda, and Matsumura (175); as was noted earlier (213, 239), the phosphorescence spectra of all three molecules are very similar, and must therefore originate in the carbonyl group. Ermolaev (89) has given spectral and lifetime data on a number of aromatic carbonyl compounds.

There has been some question about the nature of the phosphorescence of benzophenone; Ferguson and Tinson (110) found a long-lived green emission at high concentrations (~0.01 *M*) in petroleum ether, which overlapped the blue phosphorescence seen at lower concentrations. Terenin and Ermolaev (393) attribute the green emission to microcrystalline benzophenone; in ethanol, which is a better solvent for benzophenone, they found blue emission only. The emission of crystalline benzophenone was studied by Pesteil and Barbaron (284) and McClure and Hanst (245); the latter authors were able to obtain Pesteil's spectrum in material that had been stored for several weeks after purification, and they suggest that phase transitions between various of the four polymorphic forms of the crystal might be responsible for differences in the crystal spectra. This might also be the origin of the very broad green emission that is commonly observed in some samples of benzophenone, even after extensive purification. The (blue) phosphorescence origins are 24,185 (175) or 24,300 cm^{-1} (245) in EPA, and 23,800 cm^{-1} (245) in the crystal. Stockburger (380) has shown that the *second* emission band (25,179 cm^{-1}) of benzaldehyde vapor corresponds to the zero triplet level, the first (weak) band at 26,915 cm^{-1} (340) being identical with the origin of (n,π*) absorption. The small singlet–triplet separation (1736 cm^{-1}) gives rise to α-delayed fluorescence.

The phosphorescence of *benzoquinone* has been studied in the crystalline state at 20°K (355) and in the vapor (4); Kanda, Kaseda, and Matumura (175) have suggested a different interpretation of several of the low-frequency bands, and place the ^{3}U triplet origin at 18,682 cm^{-1} in the vapor, in excellent agreement with magnetic rotation results (70).

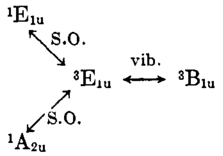
The emitting triplet state of aniline and its N-substituted derivatives is evidently of (π,π*) character; the amino group tends to reduce the phosphorescence lifetime slightly, but the rate of ISC increases by a factor of ~100, resulting in an enhanced phosphorescence yield, particularly in N-alkylamines (92).

3. *High-Resolution Spectra and Assignments*

a. Benzene

High-resolution phosphorescence spectra of benzene in rigid-glass solution were published by Dikun and Sveshnikov (65) and by Shull (353) in 1949. The vibrational analyses of both led to the assignment $^3B_{1u} \rightarrow {}^1A_{1g}$ for the pure electronic transition, which is very weak and is considered to appear through perturbation by the surrounding medium. The distinction between B_{1u} and B_{2u} character of the triplet state rested on the occurrence of one weak B_{2g} vibration in the spectrum; Ivanova and Sveshnikov (167) compared the fluorescence and phosphorescence of benzene in ethanol glass and showed that the different vibronic band intensities are consistent with the B_{1u} assignment.

Experimental measurements have also supported this assignment. Kearns (192) has discussed the results of numerous studies of substituent perturbations, polarizations, and vibrational analyses, and has shown how these, together with the theoretical treatments, are consistent with the assignment $^3B_{1u} \rightarrow {}^1A_{1g}$. The article by Kearns also contains a recent compilation of predicted locations of higher triplet levels. Albrecht (3), making use of polarization and vibrational data, proposed that the transition derives intensity from vibronic coupling in the triplet manifold and spin-orbit coupling between the two manifolds, as shown in the following scheme for the e_{2g} progression.



This mechanism gives rise to an emission with mixed polarization (in- and out-of-plane) and can account for the strongest portion of benzene phosphorescence.

Sponer, Kanda, and Blackwell (372) examined the phosphorescence of benzene in dilute solid solutions of polycrystalline cyclohexane at 4.2 and 77°K. At the lower temperature they photographed 124 bands which occurred in triplets consisting of two satellites spaced 59 and 35 cm^{-1} to either side of the middle bands. The dependence of the relative intensities of the members of the triplets on concentration (in the range 0.1 to 1% by weight of benzene in cyclohexane) led these authors to reject the participation of lattice modes as being responsible for the multiplet splitting, and they suggested instead (on the basis of further experiments on the effects of freezing rate on the spectra) that cybotactic groups consisting of different arrangements of benzene and cyclohexane molecules, or in some cases of two benzenes, can explain the observed splitting.

The study was extended to solutions in CCl_4 and dioxane at 90°K by Kanda and Shimada (177). Both of these solvents render the spectra very sharp (although less sharp than in cyclohexane) and intensify the 0–0 bands; in CCl_4 the different vibrational structure suggests that the symmetry of benzene must be reduced, probably to C_{2v}. Absorption spectra in the same solvent show that the ground state is similarly deformed. In dioxane, the benzene is apparently deformed to D_{2h} but not to C_{2v}.

b. Benzene Derivatives

The phosphorescence of *toluene* has been examined by Kanda and Sponer (182). In a very careful study at 4°K, they found the spectrum of the solid to have a lifetime of about 8 sec, and to show sharp bands together with a system of weaker bands originating at lower energy; the latter are attributed to an amorphous phase in the polycrystalline sample. Above about 27°K the phosphorescence changes in character, and at 77°K has red-shifted by 3500 cm^{-1} and is greatly shortened in lifetime. This new spectrum was found to be that of benzaldehyde, which is photochemically produced from small amounts of occluded oxygen. Kanda and Shimada (178) have found several additional bands in a more recent examination of toluene in cyclohexane at 90°K.

In spite of precautions taken to exclude oxygen, Blackwell, Kanda, and Sponer (25) found aldehydic impurity bands in the spectra of *m*- and *p-xylenes* at 4°K. The spectrum of *o*-xylene consists of two sharp systems, separated by 370 cm^{-1} and ascribed to emission from two distinct crystal phases. As in toluene, no phosphorescence was detected at 77°K. Separate "crystalline" and "amorphous" spectra are also apparent in *m*-xylene. The 0–0 bands of the *ortho*, *meta*, and *para* isomers are at 28,067, 28,301, and 28,246 cm^{-1}, respectively.

Sponer and Kanda (370) have recently analyzed the phosphorescence of mesitylene, durene, and hexamethylbenzene, both in the crystalline state at 77 and 4°K, and in EPA at 77°K. Of the three compounds, phosphorescence had been previously reported only for mesitylene (*sym*-trimethylbenzene) by Dikun and Sveshnikov (65), and by Kanda and Shimada (178). Pesteil and Zmerli (285) were unable to observe phosphorescence from the crystals at 20°K. In EPA, Sponer and Kanda (370) place the weak 0–0 band at 28,075 cm^{-1}; as in benzene, the $^3A'_1 \rightarrow {}^1A'_1$ transition is symmetry forbidden. In the polycrystalline solids, two spectra were found at 4°K (due probably to two crystalline phases); at 77°K the emission is evidently from an oxidation impurity.

The behavior of *durene* (1,2,4,5-tetramethylbenzene) is similar; the 0–0 band (27,995 cm^{-1}) appears strongly in EPA, but the true phosphorescence spectrum of the crystal is seen only near 4°K. Meyer and Astier (256) have also studied durene in hexane and in ethanol.

Hexamethylbenzene shows a somewhat different behavior (370): no phosphorescence is observed in EPA or other solvents, perhaps because of its poor solubility. At 77°K the solid gives only a weak diffuse emission, and no oxidation products could be identified. The 4°K solid spectrum begins with a well-resolved series of bands but becomes rather diffuse in its long wavelength half. The authors suggest that this diffuseness might be connected with intermolecular crowding which could result when the principal vibrations become doubly excited.

c. Polycyclic Hydrocarbons

The phosphorescence of *biphenyl* was studied by Kanda, Shimada, and Sakai (180), and more recently by Trusov and Teplyakov (394), who employed a number of different hydrocarbon matrices. The transition is symmetry allowed, $^3B_1 \rightarrow {}^1A_1$, and the 0–0 band (22,930 cm^{-1} in heptane (394)) corresponds closely with the position predicted by Iguchi (165).

Levshin and Mamedov (223) have related the phosphorescence of the *methylnaphthalenes* to three fundamental vibrations. The α and β compounds show much less difference in their phosphorescence spectra than in fluorescence or absorption.

Teplyakov (390) has studied the phosphorescence of *phenanthrene* in a hexane matrix at 77°K; 52 lines were observed, most of which had a doublet structure. The 0–0 band was placed at 21,774 cm^{-1}. Kanda and Shimada (176) studied carefully purified phenanthrene and two of its aza derivatives in EPA and petroleum ether at 90°K. In keeping with the symmetry-allowed assignment $^3B_2 \rightarrow {}^1A_1$, the 0–0 bands are quite strong.

Fluorene was studied by Kanda, Shimada, Hanada, and Kajigaeshi (179) in a cyclohexane matrix at 90°K. Comparing the phosphorescence of their synthetic fluorene with that of the commercial material, they identified dibenzofuran as an impurity in the latter; eight recrystallizations were estimated to reduce the dibenzofuran content to only 0.1 mole %. This impurity accounts for some of the spurious bands found in earlier work (142) on fluorene. Nurmukhametov and Gobov (268a) photographed 46 bands in *n*-heptane at 77°K; their interpretation of the first few bands differs from that of Kanda, *et al.* Trusov and Teplyakov (394) have recently presented phosphorescence spectra of zone-refined fluorene in several hydrocarbon matrices at 77°K.

Zmerli (416) examined the phosphorescence of *acenaphthene* both in EPA at 20°K and in the solid. In the latter, two 0–0 bands, separated by 28 cm^{-1}, are identified with the two nonequivalent sets of molecules in the acenaphthene unit cell (the crystal splitting of the singlet excited state is 141 cm^{-1}). The emission origins at 77°K are different and are ascribed to lattice defects, but may be due to impurities. Trusov and Teplyakov (394) have analyzed the 28 bands of the phosphorescence spectrum in hexane and heptane matrices.

The phosphorescence of *coronene* extends from 5000 to 6600 A, and is characterized by two very strong peaks in the green region. The spectra in hexane and heptane matrices are rather complicated and have not been completely analyzed. Shpol'skii and Klimova (350) found two very weak (symmetry-forbidden) origins at 19,425 and 19,373 cm^{-1}, and have constructed a diagram correlating the fluorescence and phosphorescence bands. They note that two intervals related to symmetrical benzene vibrations appear in the fluorescence but not in phosphorescence, suggesting that the triplet state of coronene is deformed. Bowen and Brocklehurst (27) had previously presented essentially the same spectrum; although of somewhat lower resolution, it extends farther into the red region owing to their use of different plates.

Bowen and Brocklehurst (27) were unable to locate the 0–0 band of *triphenylene* with certainty; the highest energy band they observed is a weak one at 4236 A. Most of the vibrations are unsymmetrical and some of the progressions fall off in intensity much more rapidly than others, leading the authors to suggest that vibrations of one type might be associated with a direction in which the dimensions of the triplet-excited molecule are considerably different from the singlet state.

Shpol'skii and Girdzhiyauskaite (348) found two 0–0 bands (16,906 and 16,883 cm^{-1}) in *pyrene* in a *n*-hexane matrix at 77°K. The splitting of 23 cm^{-1} is compared to the 60-cm^{-1} separation between the two series in fluorescence, but no explanation for the splitting is offered.

The two *benzpyrenes* have phosphorescence origins at 18,629 (1,2-BP) (352) and 14,670 cm^{-1} (3,4-BP) (260). Shpol'skii, Klimova, and Personov (352) photographed 150 lines of the 1,2 compound at 4°K.

d. Compounds Containing Heteroatoms

The phosphorescence of *benzonitrile, o-* and *p-dicyanobenzenes*, and all three *tolunitriles* has been analyzed by Takei and Kanda (388).

Kanda, Shimada, and Takenoshita (181) have examined the phosphorescence of *benzoic acid* in considerable detail, using five different solvents or matrices at 90°K; a spectrum previously published by Pyatnitskii (312) is presumably due to impurities. The authors also studied *methyl benzoate* and *benzamide.* The lack of a vibration characteristic of the carbonyl group in the phosphorescence suggests that the triplet state is (π,π^*). Benzoic acid and methyl benzoate are evidently deformed in a benzene matrix.

Azumi (9a) found the phosphorescence intensity of the *naphthols* to be sensitive to the solvent matrix; no emission was detected in *n*-hexane, petroleum ether, of carbon tetrachloride unless ~1% of ether was added; ether alone was also suitable. More structure is apparent in β-naphthol (13 bands) than in the α derivative (six bands). The 0–0 bands are at 20,550 (α) and 21,155 cm^{-1} (β).

Heckman (142) examined the phosphorescence of a number of heterocyclic molecules and succeeded in correlating most of the observed bands with known vibrational frequencies. The 0–0 bands of fluorene, carbazole, dibenzofuran, and dibenzothiophene are nearly coincident, indicating that the triplet state in these molecules is of (π,π^*) character.

Shimada has recently analyzed the spectrum of *pyrazine* (344) in five different media at 90°K; his interpretation of one of the bands is different from that of Goodman and Kasha (128). In benzene, the molecule is apparently deformed to C_{2v} symmetry; doublet splitting is noted in this and other polycrystalline media. The same author has also studied *pyrimidine* in different solvents (345).

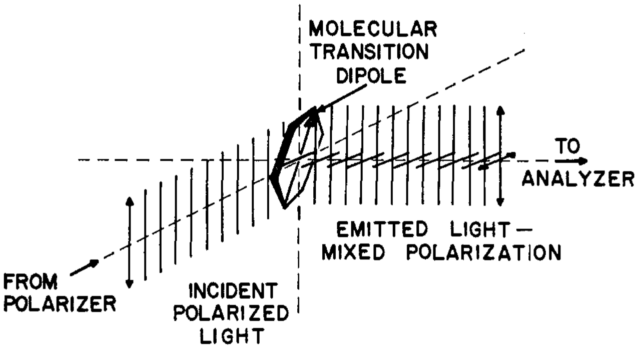


Figure 6.—Method of relative polarization measurement. The molecules are randomly oriented, but presumed to remain stationary during the lifetime of excitation. Those molecules that are oriented so as to bring the absorbing transition dipole into coincidence with the electric vector of the polarized incident light are preferentially excited; the emitted light will therefore come mostly from these selected molecules and will be of mixed polarization, analyzable into the two components indicated in the figure, where in this case the greater amplitude of the vertical component indicates a coincidence of the directions of the absorbing and emitting transition dipoles.

4. Polarization of Phosphorescence

a. Relative and Absolute Polarization Measurements

Most studies of emission polarization in complex molecules have sought to establish the direction of the transition dipole moment relative to that of a certain absorption band or a different emission band. In Figure 6, molecules whose transition directions are parallel to the indicated component of the exciting light (which must be sufficiently monochromatic to restrict its absorption to one electronic absorption band) will be strongly excited, and their emission, viewed at right angles to the exciting beam, will be resolvable into two oppositely polarized components of intensity $I_{\parallel}$ and $I_{\perp}$; other, less favorably oriented molecules, will absorb less light and contribute less to the total emission. These two observed intensities define the degree of polarization P, which can be related (222, 281) to the angle θ between the absorption and emission transition moment vectors.

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{3\cos^2\theta - 1}{\cos^2\theta + 3}$$

Most molecules of interest have a symmetry such that θ is either 0 or 90°, resulting in predicted P's of $+{}^1/_2$ and $-{}^1/_3$, respectively. These figures represent limiting values that are never achieved in practice, however. Partial depolarization can result from many causes, such as optical inhomogeneities in the medium or its container, deviations from random molecular orientation (including that produced by the use of very intense exciting light (374)), intermolecular excitation transfer, molecular motions, etc. Thus the observed absolute magnitude of P frequently has little meaning (although changes in P with excitation wavelength, concentration, etc., may be significant), and relative polarizations are usually decided to be "parallel" or "perpendicular" depending on whether P turns out to be positive or negative, respectively. The validity of this may be very questionable if P is not close to one of its limiting values, or if the absorption band serving as a reference contains appreciable vibronic components of mixed symmetry. Despite these limitations, the method has yielded much important data (107, 117), and under the name "polarized photoselection" has recently been discussed by Albrecht (2), who has applied the principle to a number of diverse problems. A recent paper by Kalantar and Albrecht discusses the polarization of electronic transitions in derivatives of benzene (174a).

By *absolute polarization* is meant the direction of the transition moment with respect to a set of orthogonal molecular axes, customarily designated L, M, and N, corresponding (where applicable) to the long and short (in-plane) and perpendicular axes, respectively. The result is independent of any assumptions regarding the polarization of other transitions. In order to determine the absolute polarization of an emission, the molecule must be oriented in a crystal in a known way. The intensities of the emission components viewed parallel to the three orthogonal crystal axes will be proportional to the squares of the projections of the transition moment vector on these axes, and the absolute direction of the moment with respect to the molecular axes can be determined by a simple transformation. The use of crystals presents several difficulties; the structures of many are not completely known, and the morphologies of others render them unsuitable. It must always be remembered that the emission properties of crystals are not necessarily those of the molecule (155), and the presence of defects or impurities may seriously affect the phosphorescence measurements. Fortunately, techniques for studying the spectra of aromatic hydrocarbons in the crystalline state have developed rapidly in recent years.

Partial orientation of sufficiently polar or unsymmetrical dyes can often be accomplished by adsorption onto stretched films of cellophane (168, 257, 303) or polyvinyl alcohol (68). Molecules that can be produced by photochemical means may be obtained in an oriented condition simply by using polarized light to bring about the photoreaction (1a, 214).

b. Phosphorescence Polarization of Aromatic Hydrocarbons

Long before the triplet character of phosphorescence was realized, Pringsheim and Vavilov (305) found that the "long wave phosphorescence" of esculin is polarized differently than the emission from its singlet excited state (in this case "α-phosphorescence"). This property was found to be common to a number of dyes by other workers (113, 123, 169, 306, 386). In some cases, phosphorescence has been found to be unpolarized, although the S* → S emission was polarized: dyes in polymethyl methacrylate (210), fluorescein in boric acid (221), and metal chelates (401) are examples.

In aromatic compounds, the allowed singlet–singlet (π,π*) transitions are all polarized in the plane of the rings; moreover, the different bands (*e.g.*, ^1L_a, ^1L_b, ^1B_b, . . ., etc. in the Platt (292) notation) could be polarized at right angles to one another. Thus if the phosphorescence is found to be polarized opposite to all of these absorption bands, then the S–T transition must have most of its intensity in a direction *perpendicular* to the rings (*i.e.*, along the molecular direction *N*). Williams (406) obtained this result for phenanthrene, but found what appeared to be short-axis (*M*) polarization in naphthalene. Naphthalene is complicated in that its ^1L_b transition, though orbitally allowed, gains much of its intensity from a b_{1g} vibration, and is thus of mixed character (109). Krishna and Goodman (207) found that the phosphorescence of naphthalene is polarized out-of-plane. According to Czekalla, Liptay, and Döllefeld (55), *N*-polarized components account for about two-thirds of the total T–S intensity; a somewhat smaller proportion of out-of-plane intensity has been reported for benzene (1). Studies of these and other hydrocarbons by Krishna and Goodman (207), Dörr and Gropper (66, 136), El-Sayed (78), and Azumi and McGlynn (10) have all indicated predominant *N*-polarized intensity in phosphorescence. The compounds studied were fluorene (66), naphthalene (55, 78, 152, 207, 406), phenanthrene (10, 78, 136, 207, 406), anthracene (152), pyrene (152), chrysene (66, 78, 152, 207), triphenylene (66), coronene (66, 78), and picene (207). Azumi and McGlynn (10) examined the polarization of individual vibronic components of phenanthrene phosphorescence, and found that certain of these bands represent a (minor) contribution of *M*-polarized intensity to the transition; this is compatible only with a ^3L_a assignment for the triplet state in this molecule. The phosphorescence of several hydrocarbons in crystalline benzophenone was investigated by Hochstrasser and Lower (152), but incomplete knowledge of the host crystal structure precluded obtaining full polarization data. The results confirm the importance of out-of-plane intensity in hydrocarbon T–S transitions; naphthalene, however, emits completely depolarized phosphorescence in this host, although the T–T absorption spectrum of the same crystal is highly polarized. Chaudhuri and El-Sayed found that naphthalene and phenanthrene and their deuterated analogs dissolved in biphenyl crystal show the *N*-polarized phosphorescence; in durene, however, a predominance of long-axis polarization is observed (37a). These results indicate that host crystal effects can significantly alter the phosphorescence mechanism.

Olds (271) examined the polarized phosphorescence of a single crystal of hexachlorobenzene, which possesses an unusually detailed spectrum for a pure crystal. Analysis of the 36 bands suggested that the molecular symmetry must be D_{3d} rather than D_{6h}; the resulting triplet assignment is $^3A_{1u}$, which corresponds to the $^3B_{2u}$ state of benzene, rather than the generally accepted (1, 167) $^3B_{1u}$ assignment (but see Craig's remarks (47a)). The polarization is mainly *N*, but considerable in-plane intensity is evident.

c. Phosphorescence Polarization in Heterocyclic Compounds

Phosphorescence polarization measurements have been of considerable importance in differentiating between π,π* and n,π* character of phosphorescence in compounds containing heteroatoms. In nitrogen heterocyclics, emission from an (n,π*) state, besides having short lifetime ($\sim 10^{-2}$ sec), is polarized in the molecular plane due to spin–orbit mixing with allowed (π,π*) transitions (45, 357). On the other hand, emission from a (π,π*) triplet level should have a phosphorescence lifetime of several seconds and should be polarized perpendicular to the molecular plane due to spin–orbit mixing with both σ,π* and n,π* allowed transitions (82). Krishna and Goodman (207) discussed the influences that different perturbing states would be expected to have on T–S transitions in nitrogen heterocyclics, and showed that the phosphorescence of pyrimidine and pyrazine is polarized predominantly in-plane (and parallel to the N–N axis in pyrazine).

Dörr and Gropper (66, 136) have made relative polarization studies of a large number of polycyclic azines: 1- and 2-azanaphthalene (quinoline and isoquinoline), 1,4-diazatriphenylene (dibenzoquinoxaline), 9,10-diaza-1,2,3,4-dibenzanthracene (1,2,3,4-dibenzophenazine) (66), 4- and 9-azaphenanthrenes (7,8-benzquinoline and phenanthridine), and 4,5-, 1,8-, and 1,4-diazaphenanthrenes (*o*-, *m*-, and *p*-phenanthroline, and benzquinoxaline, respectively) (136). The phosphorescence is always directed *out-of-plane*, corresponding to π,π* triplets. Similar conclusions were obtained for 1,4-diazanaphthalene (quinoxaline) by El-Sayed and Brewer (82), in agreement with the relatively long observed lifetime of phosphorescence in this molecule. In acetophenone, benzophenone, and anthrone, the phosphorescence was assigned to an (n,π*) process by Krishna (205).

5. *Singlet–Triplet Absorption*

Sklar (366) first observed the very weak absorption bands around 3400 A in a 20-cm path of liquid benzene and assigned them to an intercombination process on the basis of their low intensity. These bands were also studied by Lewis and Kasha (219) and by Pitts (288), who measured their intensities and wavelengths.

Using the oxygen-perturbation method, Evans presented S–T absorption spectra of benzene in the liquid (104) and vapor (105) phases and found (102) that the absorption (in a 50-cm path of liquid benzene) disappears if the solution is deoxygenated by flushing with nitrogen gas. Subsequently, Craig, Hollas, and King (49) reported no absorption in this region in a 2250-cm path of benzene that had been carefully deoxygenated! These authors estimate that the true oscillator strength of the S–T transition in benzene must be less than 7×10^{-12} (corresponding to a natural lifetime of at least 700 sec); the validity of this result has been questioned (408), but contrary experimental results have not been presented. It is not yet known whether other S–T intensities have been similarly overestimated, and more experiments along these lines are needed. It seems unlikely, however, that trace oxygen effects are important in molecules containing heavy atoms, nonbonding electrons, etc., in which intercombination is already facilitated.

Singlet–triplet absorption has found its greatest use in investigations of spin–orbital perturbation effects. In compounds containing heteroatoms, the action of solvent and substituent perturbation has been used to assign n,π^* character to the triplet states of *p*-benzoquinone (209) (confirming Sidman's (355) earlier assignment in the crystal) and pyrazine (128, 146).

Goodman and Krishna (206) showed that the $T \leftrightarrow S_0$ radiative transition could be enhanced in heterocyclics having two or more (n,π^*) states. This enhancement is thought to be due to mixing of triplet character into the ground state. These systems have strong triplet–triplet absorption between the *plus* and *minus* levels of the two n,π^* states. As a result, the proposed mixing causes strong radiative perturbation in the $T_1 \leftrightarrow S_0$ transition. El-Sayed (76a) pointed out that such an effect can explain the fact that the $T_1 \leftrightarrow S_0$ absorption of pyrazine in the vapor phase (86) is at least ten times stronger than that of pyridine (56a). Evans' use of high-pressure oxygen to intensify the S–T absorption (104, 105) has proved of value in locating the triplet levels of a number of molecules that do not phosphoresce (*e.g.*, *trans*-stilbene, diphenylacetylene, 9-nitroanthracene, etc.); conversely, he was unable to verify the very weak absorption reported to occur in the 3130–3190-A region in thiophene (275). Oxygen-enhanced S–T absorption in *pyridine* placed the triplet state of that substance at 29,650 cm^{-1} (105), after an absorption previously reported (317) was shown to be that of pyrazine impurity (32).

Weak absorption bands, presumed to be of T–S character, have been reported in a number of aliphatic ketones, including glyoxal and its deuterated analog (29), camphorquinone (113), and biacetyl (114, 354).

The lowest S–T absorption of formaldehyde vapor is due to an n,π^* transition. It has been studied extensively (30, 46, 47, 320) and has been extremely important in characterizing this molecule. Kanda, Kaseda, and Matsumura have recently examined the S–T absorption of benzaldehyde, acetophenone, and benzophenone (175); the oscillator strengths are all *ca.* 10^{-7}, and the presence or absence of oxygen has no apparent effect.

Dijkgraaf and Hoijtink (62) point out that the energies of S–T transitions should be relatively unaffected by the solvent medium, since solvent effects are based on Coulombic interactions while triplet-excited molecules interact with their surroundings mainly through exchange forces. Forster, however (114), found that different light-atom solvents had parallel effects on the intensities of the $S_0 \leftrightarrow T_1$ and $S_0 \leftrightarrow S_1$ absorption bands of biacetyl. An indirect method of observing $T \leftrightarrow S_0$ absorption has been recently reported by Avakian, Abramson, Kepler, and Caris (8). In this method a triplet *excitation spectrum* of an anthracene crystal was measured by observing the intensity of blue fluorescence (resulting from triplet–triplet annihilation) as a function of the wavelength of the exciting light, using intense red light of variable wavelength. By means of polarizing filters, they were able to determine that this absorption contains a sizable out-of-plane component, in agreement with previous polarization results on the phosphorescence of other related hydrocarbons (10, 66, 78, 136, 207).

Magnetic rotation experiments have been used to measure $T_1 \leftrightarrow S_0$ absorption in several heterocyclic compounds (70). Applying an axial magnetic field causes the $T \leftrightarrow S$ transitions to rotate linearly polarized light. The experiment is simple, at least in principle. A polarized beam passes through the sample and a crossed analyzer. The phototube behind the analyzer receives no light as long as the field is off, and the frequencies of light are not in the $T_1 \leftrightarrow S_0$ absorption region. As soon as the magnetic field is turned on and the light frequency is in the $T_1 \leftrightarrow S_0$ absorption region, the magnetic and electric vectors of the polarized light passing through the sample are rotated, permitting light to pass through the analyzer to the photomultiplier; the resulting output signal depends on the $T_1 \leftrightarrow S_0$ absorption cross section as well as the magnitude of the applied magnetic field.

6. Perturbation of S–T Transitions

a. Effects on Lifetime and Yields

The work of Weissman (411), McClure (124, 240, 244), Kasha (185), and others established the general nature of the "heavy-atom" effect on spin–orbit interaction in organic molecules. These studies attempted to correlate atomic numbers of spin–orbit coupling coefficients of the perturbing species with changes in intersystem crossing ratio $\chi = \Phi_T/\Phi_F$, phosphorescence lifetimes, or intensity of S → T absorption. An example of the effect of adding successively heavier atoms to naphthalene is shown in Table V. The perturbing action of group IV elements in tetraphenyls has been shown by La Paglia (211, 212); he reports a maximum extinction coefficient of 4–5 for the S → T absorption of lead tetraphenyl (212), probably the largest ever observed for this type of transition.

TABLE V

EFFECTS OF DIFFERENT α-HALOGEN SUBSTITUENTS ON THE EMISSION PROPERTIES OF NAPHTHALENE (FROM ERMOLAEV AND SVITASHEV (91))

Atom	Φ_F	Φ_T	χ	K_{ISC}
H	0.55[a]	0.051	0.093	1×10^5
F	0.84	0.056	0.068	2×10^5
Cl	0.058	0.30	5.2	1.5×10^7
Br	0.0016	0.27	164	5×10^8
I	<0.0005	0.38	>1000	$>3 \times 10^9$

[a] Luminescence yields are based on the absolute yield of naphthalene determined by Gilmore, Gibson, and McClure (124).

Spin–orbital perturbation can be brought about by a heavy-atom constituent of the molecule itself, or *intermolecularly* by heavy atoms in the environment, either by adsorption on a suitable surface (44) or more commonly from the use of a halogenated solvent. Kasha (185) observed a marked enhancement of the S → T absorption (giving rise to a yellow color) in chloronaphthalene in the presence of ethyl iodide; this effect has recently been studied in greater detail, in a variety of aromatic systems (248). A corresponding effect on phosphorescence emission has also been noted (123). Soviet workers have reported an increase in the phosphorescence/fluorescence ratio of phenanthrene in alcohol–KI glass (413), and decrease in the fluorescence yields and lifetimes of various compounds in the presence of iodide ion (26, 199).

Zanker and Koerber (412) have noted that the enhancement of phosphorescence in polyhalogenated dyes is sensitive to the location of the halogen substituents. Roy (332, 333) found that S → T absorption in toluene is enhanced least effectively by *para*-substituted halogen. However, in these critical experiments, impurity effects should always be questioned.

Intra- and intermolecular heavy-atom interactions have been termed "internal" and "external" by McGlynn (344), whose group has made extensive studies of heavy-atom perturbation, particularly of the external type (248).

Comparing the magnitude of the perturbing effects of a large number of alkyl halide solvents on S → T absorption intensity in chloronaphthalene, McGlynn, Sunseri, and Christodouleas (252) have shown that the degree of absorption enhancement parallels the electron-donor ability of the solvent (in any series of solvents containing the same halogen atom), and they present evidence that formation of a charge-transfer complex (with the alkyl halide acting as donor) is necessary to induce the S–T mixing responsible for the intensity of intercombination bands. According to their experiments and calculations, *external* perturbation is more effective when *internal* perturbation is already present.

Spin–orbit perturbation is expected to affect both the rate of intersystem crossing (k_{ISC}) and the probability of the S_0–T_1 intercombination ($k_P + k_{QP}$). The data of Ermolaev and Svitashev (91) indicate that the two processes are about equally sensitive to internal perturbation (see Table V), but McGlynn, Daigre, and Smith (249) conclude that k_{IS} is more affected by external perturbation in rigid glasses. More recent results indicate that k_P is affected the most by intermolecular heavy-atom effects in halogenated solvents. The heavy-atom effects of the acceptor on the observed phosphorescence lifetime of the donor in charge-transfer complexes of tetrahalonaphthalene with aromatic hydrocarbons is found (71) to be the result of a decrease in the radiative lifetime alone. Phosphorescence lifetime measurements of naphthalene and all four of its α-halogen derivatives in each of the solvents EPA and propyl chloride, bromide, and iodide have been made by McGlynn, Reynolds, Daigre, and Christodouleas (251). They make further comparisons of the relative efficiencies of the various modes of heavy-atom interaction and find that *external* perturbation increases k_P more than k_{PQ}, while *internal* perturbation affects k_{PQ} only slightly, if at all, more than k_P.

A twofold increase in the S → T absorption intensity of α-chloronaphthalene in ethyl iodide was brought about by increasing the pressure to 3644 atm; Robertson and Reynolds (328) attribute the pressure effect to an increase in the collision frequency between solvent and solute, rather than to decreased intermolecular distance brought about by the compression. Sirkar and Roy (365) report enhanced S → T absorption in benzene liquid, compared to the vapor. This effect is much more marked when a heavy atom substituent is present.

Evans' work on oxygen enhancement of S → T absorption is well known (104, 105). He also found paramagnetic NO to be an efficient perturber; S → T absorption bands have about the same wavelengths under O_2, NO, and heavy-atom solvent perturbations (62, 105). Hoijtink and co-workers (62, 158) discussed this effect on the basis of weak exchange interactions between the triplet state of benzene and the ground state of the paramagnetic perturber. In the presence of oxygen (but not heavy-atom perturbation), naphthalene shows a second absorption band (62, 63) slightly above the $\mathrm{T}_1 \leftarrow \mathrm{S}_0$ absorption in energy; this new band is assigned to a simultaneous absorption by naphthalene and oxygen. This assignment would support Hoijtink's theory of the perturbation of the triplet state. However, if it is assigned to a charge-transfer transition between the aromatic molecule and the perturber, it would support the theories proposed by Murrell (262) and Tsubomura and Mulliken (395). These workers propose that the intensification of the singlet–triplet absorption by a perturber is due to intensity-borrowing from the charge-transfer transition in the complex. The relative importance of the exchange or the charge-transfer mechanism in perturbing the $\mathrm{T}_1 \leftrightarrow \mathrm{S}_0$ transition is still an open question. Apparently it would depend on the system as well as the orientation of the two molecules. Robinson (321, 326) believes that, although a number of mechanisms for the heavy-atom effect in radiative transitions can be thought of, a second-order process, which involves electrostatic interaction (either of the charge transfer or exchange type) with the solvent as well as spin–orbit interaction in the solvent, is of dominant importance. He used an exchange mechanism (321) similar to that of Hoijtink to explain the heavy-atom effects of rare gases on the phosphorescence lifetimes of deuterated aromatics. The exchange interaction enables the aromatic $\mathrm{T} \leftrightarrow \mathrm{S}_0$ transition to borrow intensity from allowed transitions of the solvent (allowed because of the strong spin–orbit coupling in the rare gas atom). An alternative mechanism has been proposed by Murrell (262) in which the $\mathrm{T}_1 \leftrightarrow \mathrm{S}_0$ transition borrows its intensity from charge-transfer transitions which themselves borrow intensity from S–S allowed transitions of the aromatic molecule.

There are numerous experimental indications pointing to the involvement of *charge-transfer* (CT) interactions in spin–orbital perturbation processes, as theoretical studies predict. The experiments of McGlynn and co-workers (251, 252) have been alluded to above. The phosphorescence of naphthalene, phenanthrene, and other hydrocarbons is reduced both in intensity and lifetime in complexes with 1,3,5-trinitrobenzene and other acceptors (54, 55, 56, 153, 247). Christodouleas and McGlynn (42) have found that complexing with trinitrobenzene increases the value of the ISC ratio by factors of 30 and 75 for naphthalene and acenaphthene, respectively. Other experiments of McGlynn and co-workers (252) have been alluded to above. They have also noticed that the phosphorescence decays of all the perturbed naphthalenes (251) are nonexponential, and point to this and other results as indicative of (partial) CT complex formation. Evans (105) has noticed that the oxygen-perturbed $\mathrm{S} \rightarrow \mathrm{T}$ absorption of benzene in the vapor phase shows a strong 0–0 band, suggesting a reduction in symmetry that might be a result of complexing with oxygen. Finally, Dijkgraaf, Sitters, and Hoijtink (63) have detected a second absorption band in oxygen-perturbed naphthalene solution which they ascribe to a simultaneous absorption involving both the oxygen and hydrocarbon molecules; the band was absent in heavy-atom perturbed naphthalene, and its intensity was proportional to the concentration of naphthalene and the pressure of the oxygen.

b. Effects on Phosphorescence Polarization

McClure (240) has shown that chemical substitution of a halogen for one of the hydrogen atoms of an aromatic hydrocarbon decreases the observed lifetime of the phosphorescence. This decrease in lifetime is accompanied by an enhancement of the $\mathrm{T}_1 \leftarrow \mathrm{S}_0$ absorption as well as an increase in the quantum yield, indicating that the heavy atom is greatly enhancing the $\mathrm{T}_1 \rightarrow \mathrm{S}_0$ radiative transition probability.

Recently, several workers (55, 67, 84, 280, 336) using the method of photoselection, have independently examined the changes in the polarization characteristics of the emission that accompany the changes in lifetime on halogen substitution. The study has recently been extended to absolute polarization measurements of these halonaphthalenes in biphenyl crystals (37a). Pavlopoulos and El-Sayed (280) found that the spectrum of each halo derivative is composed of two subspectra, I and II. Subspectrum I is out-of-plane polarized and is similar in structure and polarization to the naphthalene spectrum. Subspectrum II is in-plane polarized and vibronically, as well as spin orbitally, induced and is absent in the phosphorescence spectrum of naphthalene. El-Sayed (80) has discussed a number of possible mechanisms that might explain the occurrence of the two subspectra. The intramolecular heavy-atom effects are explained as follows.
1. Subspectrum I results from perturbation of the lowest triplet state by out-of-plane states (*e.g.*, (σ,π^*)).
2. Subspectrum II results from the following perturbation scheme.

$$\begin{tikzcd}
 & & \mathrm{S}_{\sigma,\pi} \arrow[ddr, "\mathrm{S.O.}"] & \\
 & \mathrm{S}_{\sigma,\sigma^*} \arrow[ur, "\mathrm{Vib.}"] & & \\
\text{or} & & & \mathrm{T}_{\pi,\pi^*} \\
 & \mathrm{S}_{\pi,\pi^*} \arrow[dr, "\mathrm{S.O.}"'] & & \\
 & & \mathrm{T}_{\sigma,\pi^*} \arrow[uur, "\mathrm{Vib.}"'] &
\end{tikzcd}$$

3. Conjugation of the $p\pi$ electrons of the halogen with the π system of the aromatic ring results in one-center spin–orbit terms on the halogen in both mechanisms I and II if the σ orbitals involve the carbon–halogen bonds. This explains the sensitivity of the lifetime to the atomic number of the halogen.

The two subspectra are found to be similar in intensity (the intensity of subspectrum I is ~$^1/_4$ that of subspectrum II) even though the appearance of one is a result of a first-order interaction while the other is a result of a second-order interaction. This has been explained by the fact that the $S_{\sigma,\sigma}$ or $S_{\pi,\pi^*} \rightarrow S_0$ transitions (responsible for subspectrum II) have radiative powers which are an order(s) of magnitude larger than the radiative powers of $S_{\sigma,\pi^*} \leftrightarrow S_0$ transitions (responsible for subspectrum I).

It has been pointed out (79) that intramolecular halogen atom effects on the $\pi^* \rightarrow n$ phosphorescence process should be vanishingly small. This is due to the fact that the resulting spin–orbit terms in halogenated carbonyls have at most (when the halogen is iodine) values comparable to those present in the parent carbonyl itself. The observed heavy-atom effects in aromatic hydrocarbons are the result of the relatively weak radiative spin–orbit perturbation present in the parent hydrocarbons. If the spin–orbit perturbation between π,π^* states is nonvanishing or the σ,π^* transitions have stronger radiative power, the radiative lifetime of the aromatic hydrocarbon would have been orders of magnitude shorter, and heavy-atom effects would not be observed (79, 80).

7. *Triplet–Triplet Absorption in Rigid Medium*

Vavilov and Levshin searched for "absorption of the metastable state" in dyes in 1926, but were unsuccessful. Such absorption was detected by Lewis, Lipkin, and Magel (221) in a boric acid glass containing fluorescein; from the decrease in $S_1 \leftarrow S_0$ absorption, they estimated 75% conversion of the dye to its "metastable" species. A similar absorption was observed in diphenylamine (220).

The first comprehensive survey of T–T absorption was undertaken by McClure (241), who found one or more bands in ten different hydrocarbons and derivatives. Craig and Ross (50) extended this work to several other hydrocarbons and quinolines, and presented more complete spectra and corrected intensity data which suggest an orbitally allowed character for this type of transition. Naphthalene, phenanthrene, and anthracene give very clear spectra, and the assignment $^3B_{2u} \rightarrow {}^2B_{1g}$ or $^3A_{1g}$ (corresponding to in-plane transition moments) was proposed. Spectra of some of the larger hydrocarbons are more complicted; chrysene and dibenzanthracene show a peculiar intensity distribution, and both chrysene and pyrene appear to have two T–T bands. No T–T absorption has been observed in benzene, aniline, phenol, hexamethylbenzene, diphenyl, or pyridine.

Accurate measurements of T–T absorption intensity are complicated by optical problems arising from the non-uniform concentration of triplet-excited species in samples of reasonable size and concentration (50, 330).

Porter and Windsor (298) observed T–T absorption in anthracene and other hydrocarbons following high-intensity flash excitation of liquid solutions. By this method, it is possible to build up high momentary concentrations of triplet-excited molecules and follow their decay by monitoring the T–T absorption; this has proved an invaluable tool in kinetic studies in solution and vapor (299). A number of new T–T absorption maxima (including that of phenanthrene vapor (300)) have been found by this method (156).

T–T absorption in aromatic ketones was studied by McClure and Hanst (245), using the flash method. Acetophenone and benzophenone have upper triplet levels at ~50,000 cm^{-1}; benzophenone shows a third triplet at 41,400 cm^{-1}. One of the transitions is probably closely associated with the carbonyl group, and, being evidently allowed, might be assigned to $^3E \rightarrow {}^3Z$ in McMurry's notation (253). The other band is probably of a more delocalized nature.

Since no spin intercombination is involved, T–T absorption connecting π,π^* states should be polarized in the plane of the aromatic rings. In naphthalene and phenanthrene, relative measurements (83) reveal predominant *L* (long-axis) polarization, leading to assignments of $^3B_{1u} \rightarrow {}^3B_{3g}$ and $^3A_1 \rightarrow {}^3B_2$ for triplet–triplet absorption in naphthalene and phenanthrene, respectively. T–T absorption in naphthalene, anthracene, and chrysene incorporated into crystalline benzophenone has been found to be strongly polarized in the molecular planes (152), with no out-of-plane absorption evident. Craig and Fischer (48) have recently examined several hydrocarbons in mixed crystals; for naphthalene in durene, the absorption polarization ratio is 1:0 (b:c′), confirming the earlier (83) $^3B_{1u} \rightarrow {}^3B_{3g}$ (long-axis) assignment.

Triplet–triplet absorption of chlorophyll pigments has been reported by several workers (38, 229, 301) in conjunction with kinetic studies in liquid solution.

Triplet fluorescence ($T_2 \rightarrow T_1$) was reported for naphthalene under the rather drastic conditions of a glow discharge (339). Intensity of the emission varies quadratically with the discharge current, and the bands are separated by about 1400 cm^{-1}. An emission which had been ascribed to triplet fluorescence of azulene in rare gas matrices (326) is now attributed to an impurity (324). The most widely studied excited triplet states have been the lowest ones and the few higher ones that can be reached by triplet–triplet absorptions in the visible region. The triplet states just above the lowest ones cannot easily be studied by emission work because of the fast internal conversion processes between the triplet levels. Study by direct absorption from the ground state is impractical both because of the forbiddeness of the T–S_0 transitions.

as well as the fact that their absorption would overlap the relatively strong S–S_0 transitions, except possibly in benzene. In the latter molecule, the weak absorption in CCl_4 observed by Ham (139) near 2600 A has been the subject of debate for many years. Platt (293) has presented arguments both in support and in opposition to the assignment $^3E_{1u} \leftarrow {}^1A_{1g}$; the origin of this absorption still requires further study.

8. *Radiative Transitions between Triplet State Sublevels; Esr Studies*

The well-known work of Lewis, Calvin, and Kasha (216, 217) first established the paramagnetic nature of the triplet state. Using a Theorell-type magnetic balance, they measured a paramagnetic susceptibility very close to the theoretical value for triplet fluorescein. This work was confirmed and extended by Evans (102), who also noted that the decay of paramagnetic susceptibility of triphenylene followed the same law as its phosphorescence decay. This observation was most significant, in that it clearly showed that the decay is not a radical-recombination process, thus invalidating an alternative hypothesis of the "metastable" state.

Attempts to detect triplet-state esr absorption were without success until Hutchison and Mangum (162) observed $\Delta M = 1$ transitions in oriented mixed crystals of naphthalene in durene. In a molecule of triplet naphthalene, the threefold degeneracy of the triplet level is lifted not only by the application of an external magnetic field, but also by magnetic dipole–magnetic dipole interaction between the two unpaired electrons. Values of this *zero-field splitting* have been calculated by various workers (129, 130, 140). The $\Delta M = 1$ transitions are highly anisotropic and can only be observed when the molecules are uniformly oriented. van der Waals and de Groot (398) showed that $\Delta M = 2$ transitions, having more isotropy, are observable in rigid glass solutions of naphthalene and (134) triphenylene, coronene, and 1,3,5-triphenylbenzene. A detailed analysis of esr absorption in trigonal molecules has been given (134). $\Delta M = 1$ transitions in the same molecules (in solution) are one to two orders of magnitude less intense (410).

The esr study of naphthalene in durene by Hutchison and Mangum (164) provided the first really complete characterization of the triplet state of a hydrocarbon molecule. The fine structure of the absorption is compatible only with a ^3L_a triplet state, while the anisotropic hyperfine interaction shows that the symmetry of the state is $^3B_{2u}$ and that the molecular axes of the naphthalene and durene molecules are parallel. A recent study of triplet phenanthrene in biphenyl has revealed a discrepancy between the orientations of the guest and host molecules in that system (31). Vincent and Maki (397) found the esr spectrum of irradiated *quinoxaline* (1,4-diazanaphthalene) in durene to be very similar to that of naphthalene, and their assignment for the triplet state is also ^3L_a. Coupling of the two N^{14} nuclei with nearby protons is reflected in the hyperfine structure.

von Foerster (111) has determined zero-field splitting parameters for phenanthrene, chrysene, and fluoranthrene. Resonances have also been observed in N-ethylacridone (343). Hoijtink and his co-workers have observed esr in aromatic ions with triplet ground states (157, 174).

Esr absorption has not been reported for a triplet state of (n,π^*) character. The strong interactions between the unpaired spins in this type of state are expected to result in a large zero-field splitting, placing the spectrum outside the frequency limits that are ordinarily observed (374a). The short lifetime of this state might also introduce detection difficulties.

9. *Structure of Triplet-Excited Molecules*

"A substance which lasts for a second or two is in its own right a chemical individual, with its own set of properties" (221)—this was Lewis' rationale for presuming that molecules in their triplet states could have characteristic absorption [T → T] spectra, but it is equally applicable to the question of whether triplet-excited molecules possess an altered molecular configuration. This possibility was envisaged by Lewis and Kasha (218), whose published phosphorescence spectrum of benzene was analyzed by Redlich and Holt (316a); on the basis of Franck–Condon considerations, these authors assigned a quinoidal structure to triplet benzene. Reference has been made above to peculiarities of the high-resolution spectra of coronene (350) and triphenylene (27) which are indicative of distortion in the triplet forms of these molecules.

A somewhat different effect has been noted by Foster, Hammick, Hood, and Sanders (121), who found that phosphorescence of *p*-nitroaniline is suppressed by substitution of a methyl group adjacent to the NO_2. They suppose that the triplet state of *p*-nitroaniline shares a certain amount of quinoidal property, with the $-NO_2$ group assuming a partial negative charge, this is prevented when the NO_2 group is forced out of the ring plane by adjacent methyl substitution. On the basis of their study of α-delayed phosphorescence in adsorbed acriflavine, Rosenberg and Shombert (329) suggest that this dye is distorted in its triplet state.

Ermolaev (97) has pointed out that absorption and emission spectra should be of wider extent when the equilibrium configurations of the two states are different. He defines this width as the "Stokes loss" $\Delta\nu = \nu_{0-0} - \nu_{eq}$ in which ν_{eq} is given by

$$\nu_{eq} = \frac{\int I_\nu \nu d\nu}{\int I_\nu d\nu}$$

where I_ν is the intensity. For typical hydrocarbons, $\Delta\nu$ is found to be 1400–1900 cm^{-1} for fluorescence but 2300–2800 cm^{-1} for phosphorescence.

In formaldehyde both the singlet- and triplet-excited states are bent. The barrier for inversion doubling is somewhat higher in the triplet state (325).

The most convincing evidence for believing that deformation occurs in triplet-excited molecules comes from studies on benzene. Calculations by de Groot and van der Waals (135) have predicted that the lowest triplet state of benzene should not be a regular hexagon; their preferred configuration is the quinoidal form proposed 18 years earlier (316a). This distorted molecule, lacking trigonal symmetry, should nevertheless possess three equivalent conformations, interconvertible through an e_{2g} vibration. If the system is examined by a method that averages over a period longer than that of the interconversion process, it will still appear to have trigonal symmetry. The authors' magnetic resonance measurements are in accord with this prediction and show that the triplet state does not possess trigonal symmetry when averaged over times $<10^{-10}$ sec. In toluene, the methyl group destroys the equivalence of the conformers, and the magnetic resonance spectrum indicates the presence of two isomers.

Very recently, Nieman and Tinti (266) have shown that the phosphorescence of each of C_6H_5D and p-$C_6H_4D_2$ in deuteriobenzene matrices at 4.2°K arises from two isomers, while that of C_6H_6 or *sym*-$C_6H_3D_3$ arises from only one isomer; the fluorescence spectra of all four systems indicate the presence of one isomer in the singlet-excited state. It thus appears that the lowest triplet state of benzene possesses a twofold (but not threefold) axis of symmetry perpendicular to the molecular plane, and that the configuration lifetime of an isomeric form exceeds the phosphorescence lifetime. This last conclusion conflicts with that of de Groot and van der Waals (135) obtained from esr studies in glasses. Of course the disagreement would disappear if the lifetime of the different triplet isomers is sensitive to the type of host. These results would thus suggest that the barrier for interconversion between triplet isomers in C_6D_6 host crystals is larger than in organic glasses.

IV. BIMOLECULAR INTERACTIONS INVOLVING THE LOWEST TRIPLET STATE

A. TRIPLET QUENCHING IN FLUID MEDIA

1. Triplet Decay in Liquid Solution

The rate of disappearance of triplet-excited species in fluid solution is so dominated by radiationless processes that phosphorescence is not ordinarily observed except from the relatively few substances having high phosphorescence yields and radiative lifetimes of sufficiently brief duration to permit radiative decay to compete successfully with the other processes; biacetyl (115), benzil, and anisyl (15) are examples. All of these compounds have phosphorescence lifetimes of $\sim 10^{-5}$ sec in solution at room temperature. Parker and Hatchard have detected the phosphorescence of phenanthrene in fluid solution at 286°K; its intensity is reduced from the 77°K rigid-glass value by about 10^{-3} (277).

A general expression for the rate of triplet decay in liquids is (230)

$$-\frac{d[T]}{dt} = k_1[T] + k_2[T]^2 + k_3[T\cdot S_0] + \sum_i (k_Q)_i[M_i][T]$$

in which [T] and [S_0] denote the concentrations of triplet and unexcited species, and $k_1 = k_P + k'_{PQ_1}$, in which k'_{PQ1} is the rate constant for unimolecular quenching (*i.e.*, the spontaneous $T_1 \rightarrow S_0$ radiationless process). The last term in the equation represents quenching by impurity or other foreign molecules M_i. The decay process is most conveniently followed by Porter's method (294, 299) of monitoring the intensity of triplet–triplet absorption following excitation with an intense flash source.

The dominance of radiationless decay processes in fluid solution is usually ascribed to the increased opportunity for encounter of excited species with each other, with unexcited molecules, and particularly with quenching impurities such as oxygen. Even when special pains are taken to minimize these second-order processes, however, values of the triplet decay constant have exceeded those measured in rigid glasses, and this has led to the thought that the frequent and varied collisional contacts between triplet species and solvent molecules might themselves constitute a quenching process. Such a process would be first order and dependent on the viscosity of the solvent (60), and indeed the earlier flash studies on triplet decay in solution did indicate a strong viscosity dependence for k_1 (299). Further work, however, has given rise to serious doubts about, or at least qualification of, this apparent diffusion-limited character of k_1.

In a series of experiments which were designed to minimize the effect of second-order processes, Hilpern, Porter, and Stief (145) measured first-order rate constants for triplet decay of naphthalene, anthracene, and several halogen derivatives. They found two distinct types of behavior at high and low temperatures (viscosities). At high viscosities the rate of decay is almost independent of viscosity and is clearly unimolecular; a small residual temperature dependence is ascribed to an activation energy which, in anthracene (where it was most pronounced), amounted to 400 cal. At low viscosities, the decay assumed the characteristics of a diffusion-limited process, suggesting the participation of an impurity quencher.

Similar results were obtained by Stevens and Walker (379) who used a different method. They measured the decay rates of delayed fluorescence (k_{DF}); assuming that delayed fluorescence is the result of a triplet–triplet annihilation process (278) and that triplet decay is exponential, these workers showed that the relation $k_{DF} = 2k_T$ can be used to find k_T under conditions where direct observation of phosphorescence is not possible. At lower temperatures (in fluid solutions) k_T was found to approach a limiting value $k_T°$ which in two cases (pyrene and 1,2-dibenzanthracene) compared favorably with values obtained in rigid glasses at 77°K.

Jackson and Livingston (170a) found the lifetime of triplet anthracene in hexane to be independent of temperature over the temperature range 30 to $-70°$.

It thus began to appear that apparent measured values of k_1 were actually $k_1 + k_Q$ with $k_Q > k_1$, the quenching process becoming pseudo-unimolecular at low viscosities. This prompted further experiments in which particular attention was paid to minimizing oxygen and solvent impurities, and each refinement of technique yielded smaller values of k_1, with the lowest values supposedly being the most nearly "true" ones. Thus for anthracene, k_1's of 3000 (302), 1600 (237), 350 (171), 110 (156), 75 (230), and 50 sec^{-1} (145) have been reported (approximately in this chronological order). Using a chemically deoxygenated pyridine solution, Linschitz, Steel, and Bell (230) obtained an indication of an even lower rate than in a solution carefully degassed by conventional methods. More recently, Livingston and Ware (238) have obtained 30 sec^{-1} for anthracene and 0.40 sec^{-1} for naphthalene. Since k_1 is 38 sec^{-1} for anthracene in acrylic plastic at room temperature (255), it would appear that the lower values of k_1 quoted above represent a truly first-order process. This conclusion is also supported by the work of Jackson, Livingston, and Pugh (171), who found no change in the value of k_1 for anthracene (350 sec^{-1}) over a viscosity range of 0.3 to 2.4 cp, and less than a fivefold change on altering the viscosity by a factor of 3000.

The nature of the pseudo-unimolecular quenching process responsible for the higher values of k_1 is still not entirely clear. It is generally agreed that an adventitious solvent impurity is responsible, although points have been raised against this as the sole interpretation (295). Stevens and Walker (379) definitely established the presence of an impurity quencher in experiments on pyrene in liquid paraffin, and set the lower limit of quencher concentration at $2 \times 10^{-7}\ M$; other estimates range from 10^{-4} (295) to 10^{-7}–10^{-8} M (145). Oxygen seems to be the most likely culprit and is known to be an efficient quencher of the triplet state (395); an oxygen concentration of about $10^{-4}\ M$ has been shown to half-quench the phosphorescence of phenanthrene in a 77°K rigid glass, and measurements of $k_{Q(O_2)}$ give values $\sim 10^9\ M^{-1}\ \text{sec}^{-1}$ for anthracene (237, 296), naphthalene (296), and chlorophyll (229). While many workers seem to feel that their degassing procedures are sufficiently thorough to bring the oxygen concentration to too low a value to account for the observed quenching, there exists no independent analytical method for measuring very low oxygen concentrations, and one may well ask if it is possible to remove all the dissolved oxygen by less-than-drastic procedures, particularly in view of its demonstrated ability to form charge-transfer complexes with aromatic compounds (395, 409). Activation energies of the quenching process in low-viscosity solutions correspond to activation energies of diffusion, but in more viscous media they tend to be less than the values predicted by simple diffusion theory (238).

In summary, the present data suggest that the sometimes apparent diffusion-limited character of k_1 is largely an artifact resulting from quenching impurities of still uncertain nature as well as, in some cases, triplet–triplet interaction. The question is not completely closed, however, and it is quite conceivable that under special circumstances, *e.g.*, where slow torsional vibrations are active in electronic transitions, direct collisional interaction or coupling to Brownian rotation (295) might make a contribution to k_1.

Other contributions to the triplet decay rate are made by the $k_2[T]^2$ and $k_3[S][T]$ terms. The T–T quenching process has been shown to be diffusion-limited except at very low viscosities (171, 228, 302) and becomes significant only at high concentrations or high light intensities. The value of k_2 (at viscosities below 1 cp) is $1\text{–}2 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ for anthracene (302) and $1\text{–}3 \times 10^9\ \text{l}\ M^{-1}\ \text{sec}^{-1}$ for chlorophyll (229). Quenching of the triplet by ground-state molecules has not been observed in aromatic hydrocarbon solutions (for anthracene, $k_3 < 10^6\ M^{-1}\ \text{sec}^{-1}$ (230)) but might be important in chlorophyll solutions, although the previously reported value of 10^7–$10^8\ M^{-1}\ \text{sec}^{-1}$ (229) is now thought to be too high (230). The apparent high value of the activation energy of triplet quenching of retinene in glycerol (133) is thought by Dawson and Abrahamson (59) to arise from temperature variation of the hydrogen-bonded solvent–retinene complex, which they show to have a much lower value of k_{ISC} than free retinene.

2. Metal Ion Catalyzed Triplet Decay in Solution

Porter and Wright (302) measured rate constants of triplet naphthalene quenching by metal ions in water and ethylene glycol. They found that diamagnetic ions have no appreciable effect, while paramagnetic ions all quench the triplet state, *but with varying efficiencies that are apparently unrelated to the paramagnetic susceptibility.* They suggest a "catalyzed spin conservation" mechanism that is quite distinct from the more familiar magnetic perturbation of spin–orbital coupling. This mechanism predicts that singlet–triplet intercombination will be allowed in a collisional process involving a molecule or ion with multiplicity greater than unity. They show that on statistical grounds, all paramagnetic molecules should be equally effective in quenching triplet states; observed differences must therefore arise from such causes as different stabilities of the collision complexes and possibly steric factors.

Linschitz and Pekkarinen (228) note that the quenching constants (of anthracene) for cupric, nickel, and cobaltous chlorides are all around 10^8 M^{-1} sec^{-1}, while k_Q for manganous ion is less by a factor of 10^{-2}, and for rare earth chlorides still less by another order of magnitude. The addition of water to tetrahydrofuran solutions reduces the quenching rates by 10^{-2}. Acknowledging Porter and Wright, they point out that some diamagnetic quenchers have rates comparable to that of oxygen, and that transition metal salts are also known to be effective in *fluorescence* quenching, in which $MnCl_2$ is also anomalously weak. In fluorescence quenching, paramagnetic influence on the rate of internal conversion has not been completely excluded, but it is thought to be unlikely—see footnote 17 of ref 228. Linschitz and Pekkarinen propose a charge-transfer mechanism, in which the different configuration of the ionic state of the complex might set up strong vibrations that facilitate intersystem crossing. This is supported by the finding (373) that the rates at which copper complexes of ethylenediamine, pyridine, and phenanthroline catalyze triplet decay depends on the particular complex, and that their quenching ability parallels their tendency to enter into charge-transfer reactions.

3. *Triplet Decay in the Gas Phase*

Dikun (64) estimated that triplet-excited molecules in phenanthrene vapor survive $\sim 10^5$ collisions before undergoing "reverse" ISC and α-delayed fluorescence, which was the only significant pathway of deactivation reported in this experiment.

In their vapor phase study of aromatic hydrocarbon triplet states, Porter and Wright (302) found that the rates of intersystem crossing (both $S^* \rightarrow T$ and $T \rightarrow S_0$) are independent of pressure under ordinary conditions.

The vapor phase decay of naphthalene and anthracene can be explained (296) entirely in terms of second-order triplet–triplet quenching, which appears to be a highly efficient process; the observed values of k_2 closely approach the collision rates ($\sim 10^{11}$ sec^{-1}) under the conditions of the experiment. Quenching by oxygen was found to occur at only about 1% of the collision rate and is thus about as efficient as in hexane solution (299).

B. ENERGY TRANSFER INVOLVING THE TRIPLET STATE

1. *Excitation Transfer*

Radiationless electronic energy transfer between molecules has been a well-known phenomenon since the work of Perrin (283), but early attempts to establish the occurrence of intermolecular transfer of triplet excitation yielded conflicting results. Thus Lewis, Lipkin, and Magel (221) reported the insensitivity of fluorescein phosphorescence to concentration quenching, and Feofilov (106) found the polarization of phosphorescence from several dyes to be constant throughout the entire period of decay. On the other hand, concentration quenching of dye phosphorescence was observed by a number of Soviet workers (224, 385, 337a), and triplet transfer was suggested as a possible mechanism to explain quenching in metal–organic complexes (401) and the phosphorescence quenching of benzene by iodobenzene (110). Unequivocal demonstration of intermolecular radiationless T → T transfer was first accomplished by Terenin and Ermolaev (392) in 1952 and has since been confirmed and studied in rigid-glass solutions, liquids, vapors, and crystals.

Aside from the trivial case of reabsorption of emission by a nearby molecule, the most familiar intermolecular energy-transfer process is that responsible for long-range (~40 A) singlet excitation transfer; it has been discussed by Perrin (282), Förster (116, 117, 119), and Dexter (61). This process can be regarded as a coupling of optical transitions of the donor and acceptor molecules, resulting in simultaneous radiationless deactivation of the donor and excitation of the acceptor. The probability of transfer depends on an expression (see ref 119 for a brief review) containing the integral

$$\int_0^\infty f_D(\nu)\epsilon_A(\nu)d\nu$$

where $f_D(\nu)$ is the spectral distribution of the donor luminescence and $\epsilon_A(\nu)$ is the extinction coefficient of the acceptor. Transfer thus occurs with highest probability when intense (*i.e.*, electric dipole) transitions of the donor and acceptor overlap in frequency.

When excitation transfer occurs, the donor emission will be partly quenched, its normal observed lifetime $\tau_D{}^\circ$ being reduced to τ_D; these two quantities can be related to the luminescence quantum yield (for the particular transition involved) of the donor in the absence of transfer.

$$\tau_D = \Phi_D \tau_D{}^\circ$$

The rate constant for excitation transfer can be expressed as

$$k_{D \rightarrow A} = (1/\tau_D)(R_0/R)^6$$

where R_0 is the "critical distance" between donor and acceptor at which transfer and spontaneous decay of the donor become equally probable. It is doubtful, however, that experimental values of R_0 have as much meaning as is frequently attributed to them, due mainly to the effects of non-uniform distribution of active molecules and partly to the importance of multipole and exchange (see below) terms that are usually neglected.

If the donor transition is spin-forbidden, transfer by this mechanism can still be efficient if the acceptor transition is intense, overlap is good, and the triplet efficiency for triplet population of the donor is high; in this case the slower transfer rate is compensated by the longer radiative lifetime of the donor (61, 119). Examples of intermolecular $T \rightarrow S^*$ transfer have been given by Korsunskii and Faidysh (203), Ermolaev and Sveshnikova (98, 99), and Bennett, Schwenker, and Kellogg (19, 195). Coupling of an allowed donor transition with a forbidden acceptor band is not expected to be efficient, and direct intermolecular $S^* \rightarrow T$ transfer has not been reported.

If the transitions of donor and acceptor are both spin-forbidden, then the Coulomb term (responsible for long-range transfer) of the matrix element in the transition-probability expression drops out. The principal term remaining is an exchange integral which is sensitive to overlap of the electronic charge distributions of the two molecules. It is thus expected that the transfer probability will be sensitive to the relative orientation of the donor–acceptor pair, having a maximum value for a certain configuration. Roy and El-Sayed (334), using a modified photoselection method ("photoselective sensitization" (335)), showed that the configuration of the donor–acceptor pair for maximum triplet–triplet transfer in rigid medium is that for maximum charge overlap, as expected. In cases where charge-transfer complexing is possible, the configuration of maximum energy transfer is found to be that expected for the charge-transfer complex (335). Exchange interaction falls off exponentially and thus much more rapidly with distance than the $1/R^6$ dipole interaction, but the interaction can extend far enough to permit efficient triplet excitation transfer when the two triplet levels are energetically similar and over-all spin conservation holds (264).

Robinson and Frosch (326) have emphasized the importance of virtual states of the medium in excitation transfer, especially when the lowest electronic states of the solvent are close to those of the excited molecule, as in many mixed crystal experiments. Siegel and Judeikis, however, compared the efficiency of triplet–triplet transfer in various binary aromatic systems with the separation between the lowest triplet levels of the solutes and the rigid-glass solvents (saturated and unsaturated glasses were used), and found no dependence of transfer efficiency on solvent-solute triplet separation for ΔE's of $>1000\ \mathrm{cm}^{-1}$ (359).

2. Sensitized Phosphorescence in Rigid Solution

Intermolecular $T \rightarrow T$ excitation transfer is most unequivocally demonstrated in systems where the S_1 and T_1 levels of the donor are bracketed by the same two levels of the acceptor, as in benzophenone–naphthalene (see Figure 7a) which Terenin and Ermolaev (392) used in their initial study of sensitized phosphorescence.

Excitation of a rigid-glass solution of the two components with light absorbed only by benzophenone results in emission of naphthalene phosphorescence of normal lifetime. Ermolaev (87, 88, 90, 93, 94, 99, 100) has studied $T \rightarrow T$ transfer in a wide variety of donor–acceptor combinations and has published a thorough review of the subject (96). As the exchange-resonance mechanism predicts, the range of the interaction is much less than in dipole–dipole transfer; R_0 was found to be 11–14 A in 23 different systems (93). Further support for this mechanism and against the dipolar mechanism is provided by the demonstration (90, 100) that the $T \rightarrow T$ transfer efficiency is insensitive to a 1000-fold change in the intensity of the acceptor $T_1 \leftarrow S_0$ transition in naphthalene and its halogen derivatives.

Ermolaev has defined the quantity $\gamma = \Phi_A'/(\Phi_D - \Phi_D')$ as the quantum yield of sensitized phosphorescence, where the primed letters represent quantum yields of donor or acceptor phosphorescence in the presence of $T \rightarrow T$ transfer. γ can be calculated graphically from the relevant spectra (96) or determined directly from the readily measured quantum yield ratios Φ_A'/Φ_D' (which is sensitive to acceptor but not donor concentration (88, 90, 100)) and Φ_D/Φ_D'

$$\gamma = \frac{\Phi_A'}{\Phi_D - \Phi_D'} = \frac{\Phi_A'}{\Phi_D} \cdot \frac{1}{1 - (\Phi_D'/\Phi_D)}$$

Values of γ for several systems studied by Ermolaev (93) are given in Table VI; here, a distinct correlation with the phosphorescence yield of the acceptor is apparent.

TABLE VI

Acceptor/donor	Benzophenone	Phenanthrene	Benzaldehyde	*m*-Iodobenzaldehyde
Naphthalene	0.07	0.30	0.13	0.11
α-Chloronaphthalene	0.12	0.73	0.22	—
α-Bromonaphthalene	0.20	11.00	0.27	0.30

In more complex molecules such as unsymmetrical aromatic ketones, intramolecular triplet excitation transfer is frequently possible. Ermolaev and Terenin (100) investigated a number of compounds typified by phenyl naphthyl ketone, whose phosphorescence is characteristic of that portion of the molecule having the lowest triplet level, in this case naphthalene.

The lifetimes, however, are shorter than in the free hydrocarbons. Similarly, the compound Ph–CO–PH–CH_2–Naphth gives an emission resembling that of α-methylnaphthalene rather than 4-methylbenzophenone (213).

Intramolecular transfer in trypticene and tribenzotrypticene has been demonstrated in the paramagnetic resonance experiments of de Groot and van der Waals (135).

3. Sensitized Luminescence in Fluid Solution

Bäckström and Sandros (14) presented photochemical evidence for intermolecular T → T transfer in *fluid solution.* In a later study (15), they found that benzophenone can efficiently sensitize the phosphorescence of biacetyl; no biacetyl fluorescence was detected, even though both the S* and T levels of this molecule are below the triplet level of benzophenone (it should be pointed out that intersystem crossing in benzophenone is virtually complete).

In liquid or vapor phases, transfer can often occur before thermodynamic equilibrium is established between an excited molecule and its surroundings; in this case, the formulas describing exchange-resonance transfer cannot be expected to hold (119), and measurements of R_0 cease to have any physical meaning. A dependence of the transfer efficiency on the energy difference between the two triplet levels is also apparent. Sandros and Bäckström (337) measured the quenching rates of 21 compounds on biacetyl; the measured rates were found to increase with the energy difference between the triplet levels of the donor (E_T = 19,700 cm^{-1} for biacetyl) and the acceptor (quencher). With quenchers having triplet levels below 17,000 cm^{-1}, the rate becomes diffusion limited and each collisional encounter evidently results in quenching. Similar results were obtained by Porter and Wilkinson (297), who measured the triplet acceptor concentration directly. Lipsky (233) has studied triplet transfer from benzene to biacetyl in cyclohexane solution; a tenfold increase in the Φ_P/Φ_F ratio of biacetyl was noted in this system.

The demonstration of T → T transfer in vapors is a recent development. Dubois (69) used benzophenone vapor to sensitize the phosphorescence of biacetyl and found the process to be diffusion controlled. Ishikawa and Noyes (166) found that biacetyl strongly quenches the fluorescence of benzene vapor while simultaneously increasing its phosphorescence yield. Further evidence for triplet transfer to biacetyl vapor has been obtained from studies on 3-methyl-2-butanone (403), acetone (143), 2-pentanone (399), and hexafluoroacetone (28).

Sensitization of rare earth ion emission in rare earth chelates by triplet-excited aromatic molecules in solution has recently been demonstrated by Bhaumik and El-Sayed (21, 81). These workers showed (81) that the initial transfer from the aromatic molecule is diffusion controlled, and proposed the following mechanism.

$$T_{\text{donor}} \xrightarrow{\text{intermolecular}} T_{\text{chelate}} \xrightarrow{\text{intramolecular}} \text{R.E. ion} \rightarrow \text{emission}$$

A diffusion-controlled transfer from triplet donors to rare earth ions in solution has also been demonstrated (21, 144).

Crosby and his co-workers (52, 404) originally suggested that the intramolecularly sensitized rate earth emission, obtained by direct excitation of chelates, involves the transfer of excitation from the triplet state of the ligand to that of the rare earth ion. However, Kleinerman (200) has recently pointed out that Crosby's results did not exclude transfer through the singlet state of the ligand. Bhaumik and El-Sayed (22) found that the addition of a substance capable of quenching the triplet of the ligand (but not that of the free rare earth ion) brings about quenching of the ion emission without decreasing its lifetime, thus supporting the original hypothesis of the triplet transfer mechanism. The rate of the intramolecular energy transfer from the ligand to the ion is found to be 10^{10} sec^{-1} (22).

C. TRIPLET–TRIPLET ANNIHILATION; DELAYED FLUORESCENCE

The term *delayed fluorescence* (DF) has been applied to a number of emissions of diverse origin (α-phosphorescence, radical-recombination luminescence, etc.) which are spectrally identical with the normal $S_1 \rightarrow S_0$ fluorescence but exhibit a lifetime of the order of milliseconds to seconds. Preferred current usage of the expression restricts it to denote fluorescence arising from the two-photon (or -exciton) process $T + T \rightarrow S_1 + S_0$, $S_1 \rightarrow S_0 + h\nu$. This scheme was suggested by Parker and Hatchard (278) on the basis of their finding that the intensity of DF in fluid solutions of anthracene and phenanthrene varies as the *square* of the amount of light absorbed. This result has been confirmed by Stevens and Walker (379), who examined the kinetics of DF and phosphorescence in solutions of acenaphthene, pyrene, 1,2-benzanthracene, and fluoranthene in the temperature range 300–210°K. A recent review on the subject is given by Parker (276).

Some time ago, Williams (405) had reported a DF from vapors of anthracene, perylene, phenanthrene, and pyrene. The pressure dependence of the emission suggested a bimolecular mechanism, and he attributed the DF to emission from an excited singlet molecule following breakup of a long-lived dimer. Whether this is the correct explanation or whether triplet annihilation is involved is not yet certain. Azumi and McGlynn have observed DF in rigid-glass solutions of naphthalene, phenanthrene, hexahelicene (11), triphenylene (12), and pyrene (13); they were unable to detect it in anthracene, 1,2-benzanthracene, and chrysene (11). The high concentrations used and the sensitivity of these experiments to the type of solvent raises the possibility that the observed emission came from microcrystals rather than from a true solution. DF has also been reported in crystals of naphthalene (24, 371), where it is due to traces of β-methylnaphthalene impurity (376).

The simplified scheme given above predicts that DF should decay twice as fast as phosphorescence (278), but the rates observed in rigid solution (11, 12) are somewhat greater than this. Sternlicht, Nieman, and Robinson (376) have presented a detailed discussion of the kinetics of triplet annihilation in solids, and they predict two limiting types of behavior corresponding to high and low concentrations of the active species in the medium (in the case of C_6H_6 in C_6D_6, the authors find these two concentrations to be 5 and 1%, respectively). Only at low concentrations should $k_{DF} = 2k_P$; as the concentration is increased (*e.g.*, by increasing the light intensity), both phosphorescence and DF decays are expected to become nonexponential, while the intensities of the two emissions approach linear and square-root dependences, respectively, on the number of quanta absorbed. The immediate products of triplet–triplet annihilation are presumably the components of an "excimer" (387) which term is used to designate an excited dimer or complex, denoted by $[S + S]^*$. Förster and Kasper (118) first demonstrated the existence of this species in pyrene solution. It is responsible for the broad structureless fluorescence band that occurs at lower energies than the normal fluorescence in this and many other molecules at high concentrations. Delayed *excimer fluorescence* (DXF) may be observed under favorable circumstances. Stevens and Hutton (378) reported emission of this kind in liquid solutions of pyrene and noted its sensitivity to oxygen quenching. Two mechanisms whereby DXF might arise in fluid solutions can be envisaged, depending on whether the two interacting triplets form an excimer directly (279) or form an initially created excited monomer (389). Birks (23)

$$\begin{tikzcd}
 & & 2S_0 + DXF & \\
2T \arrow[r] & {[S + S]^*} \arrow[ur] \arrow[dr] & & \\
 & & S^* + S_0 \arrow[r] & 2S_0 + DF
\end{tikzcd}$$

$$\begin{tikzcd}
 & & 2S_0 + DF & \\
2T \arrow[r] & S^* + S_0 \arrow[ur] \arrow[dr] & & \\
 & & {[S + S]^*} \arrow[r] & 2S_0 + DXF
\end{tikzcd}$$

and Smith and McGlynn (368) have shown that both processes are operative in fluid solution, the first one being favored at low viscosities. The latter authors found the intensities of both the DF and DXF of pyrene solutions to vary as the square of the phosphorescence intensity under conditions where phosphorescence was measurable. The lifetimes of both emissions were half the phosphorescence lifetime. Excimer fluorescence and DXF were also observed in pyrene crystals (368), the DXF in this case varying directly with the exciting light intensity as predicted (376) for high concentrations; an earlier report (3) of DXF from a rigid-glass solution of pyrene is shown to be erroneous—the emission is evidently from microcrystals which precipitated out of a poor solvent. In solids, where DF is thought to arise from a long-range triplet transfer and annihilation mechanism (376), the above schemes have no meaning if molecular diffusion is slow. If the crystal structure favors dimer interaction (as in pyrene (155, 382)), then DXF will presumably be favored.

Stevens, Hutton, and Porter (383) detected the DF of anthracene present as an impurity in phenanthrene vapor; Parker and Hatchard (278) have made further studies of *sensitized DF* in solutions of anthracene and phenanthrene. A similar phenomenon has been observed in mixed crystals (376).

Parker and Hatchard (278) pointed out the possibility of obtaining emission of a shorter wavelength than the exciting light by using a donor species to sensitize DF in an acceptor having a higher S_1 and lower triplet state than the donor. They succeeded in demonstrating *sensitized anti-Stokes DF* in two solution systems, utilizing phenanthrene–naphthalene and proflavine–anthracene as donor–acceptor combinations in ethanol at room temperature. Muel (259a) has observed similar luminescence in which excitation of 3,4-benzpyrene by light of >5000 A produced DF in the 4000–4600-A region from auramine, fluorescein, and other dyes.

D. TRIPLET EXCITATION TRANSFER IN CRYSTALS

1. *Triplet Excitons*

The concept of the exciton in organic molecular crystals, developed by Davydov (58) and applied to aromatic hydrocarbon crystals by Craig and others (51, 243), has been eminently successful in explaining the spectroscopic behavior of the singlet-excited states of these systems. The observation of triplet excitation migration in rigid media prompted the question of whether exciton band formalism might be applicable to triplet energy transfer in crystals. This question could be answered in the affirmative *theoretically* if calculations predicted sufficiently large values of intermolecular interaction energies (between triplet-excited molecules), and *experimentally* if long-range excitation diffusion having properties consistent with exciton motion could be demonstrated or if the Davydov-type splitting could be observed from the $T_1 \leftrightarrow S_0$ absorption of single pure crystals.

In order for the exciton concept to apply, adjacent molecules in a crystal must interact with one another along at least one direction. In the singlet manifold, the principal contribution to this interaction is made by Coulombic (dipole–dipole and higher multipole) terms, and in fact excellent agreement with experimental results is achieved in some cases by means of purely classical dipole-expansion calculations. In the case of triplet-excited molecules, however, the Coulombic terms vanish, and it was originally estimated (375) that the remaining electron-exchange terms were of too small magnitude to yield appreciable triplet exciton band widths.

Very soon, however, a number of experimental studies had demonstrated triplet energy migration between (dilute) guest molecules in molecular crystals. The sensitized phosphorescence experiments of Robinson's group (86, 264, 265, 376) elucidated the nature of guest-to-guest triplet migration in mixed crystals, and provided an estimate (265) of the triplet interaction matrix element that was much larger than had been thought likely. Hochstrasser (147) demonstrated the high efficiency of triplet migration in benzophenone crystals in his emission experiments, while the magnetic resonance experiments of Brandon, Gerkin, and Hutchison (31) showed that triplet transfer in biphenyl host crystals is definitely a long-range process, and not an artifact of complexing or accidental juxtaposition of donor and acceptor molecules. Finally, Kepler, Caris, Avakian, and Abramson (197) showed that bimolecular-delayed fluorescence experiments could be interpreted on the basis of an exciton annihilation mechanism, with an annihilation rate constant of 2×10^{-11} cm^3 sec^{-1} in crystalline anthracene.

Reconsideration of the electron-exchange energy calculations has shown (191, 264) that the use of more appropriate basis wavefunctions (SCF rather than simple Slater orbitals) resulted in less rapid falloff of the exchange terms with distance. Jortner, Rice, Katz, and Choi (173) have recently presented an excellent discussion of triplet excitons in molecular crystals and have calculated the interaction integrals, exciton band structure, and Davydov splitting for crystals of naphthalene, anthracene, and biphenyl. They discuss the mechanism of exciton propagation through the crystal; the interactions between adjacent molecules are of such magnitude (5–10 cm^{-1}) as to place the rate of *exciton* migration close to the frequency of intermolecular lattice vibrations, with the result that the rate of exciton motion should be limited by scattering by lattice phonons. Singh, *et al.* (363), feel on the contrary that phonon-induced exciton scattering is not important, since the thermal activation of exciton diffusion (important for the "hopping" model of Jortner (172, 173), has not been demonstrated. The triplet diffusion rate of Jortner is too small, and the T–T annihilation rate constant is probably $>10^{-9}$ cm^3 sec^{-1}. This value is in disagreement with observation (197).

The electron-exchange contributions to the Davydov splittings of the lowest triplet states of naphthalene and anthracene are calculated (173) to be 30–40 cm^{-1}; the actual splittings of the individual vibronic bands should be $^1/_4$–$^1/_5$ of these values, in accordance with the weak coupling approximation (362). The authors show that configuration interaction between neutral and charge-transfer exciton states (39) should increase the rate of exciton migration and thus the diffusion length. A value of 10^{-10}–10^{-11} cm^3 sec^{-1} for the triplet–triplet exciton annihilation rate in anthracene was predicted, in excellent agreement with the experimental results (138, 197).

Avakian and Merrifield (9) have succeeded in making a direct measurement of the triplet exciton diffusion length in the anthracene crystal. Their value of $10 \pm 5 \times 10^4$ A is in good agreement with the calculated value of 8×10^4 A (172, 173). Experimental observation of Davydov splitting in singlet–triplet absorption has not yet been reported.

2. *Mixed-Crystal Experiments*

Excitation transfer in crystals does not differ fundamentally from that in random solution; aside from the effects of the order and symmetry on exciton motion and selection rules, the principal differences that manifest themselves experimentally arise from the high concentrations of molecules in crystals and the generally smaller energy gap between the lowest electronic states of solvent and solute in the mixed crystals of greatest interest.

By judicious choice of "host" and "guest" substances, it is possible to construct systems in which the S_1 and T_1 levels of the two types of molecules bear special energetic relationships to one another. Selective excitation of guest or host and accurate intensity measurements of the relevant emissions can then lead to at-least-limiting rate data for the various possible internal photoprocesses (150). Of the several energy schemes depicted in Figure 7, that of 7a in which naphthalene is the guest in a benzophenone crystal has been most widely studied. Cadas, Courpon, Lochet, and Rousset (37) reported sensitized phosphorescence in this system; investigating a wide range of naphthalene–benzophenone concentration ratios, they found no evidence for complex formation.

El-Sayed, Wauk, and Robinson (86) have shown that triplet excitation migration in crystals is more efficient than singlet transfer. They found that triplet energy transfer in naphthalene-h_8/naphthalene-d_8 takes place not only in the $C_{10}D_8$ host levels, but also by long-range tunneling between the $C_{10}H_8$ guest centers and impurity centers of lower concentration (from which

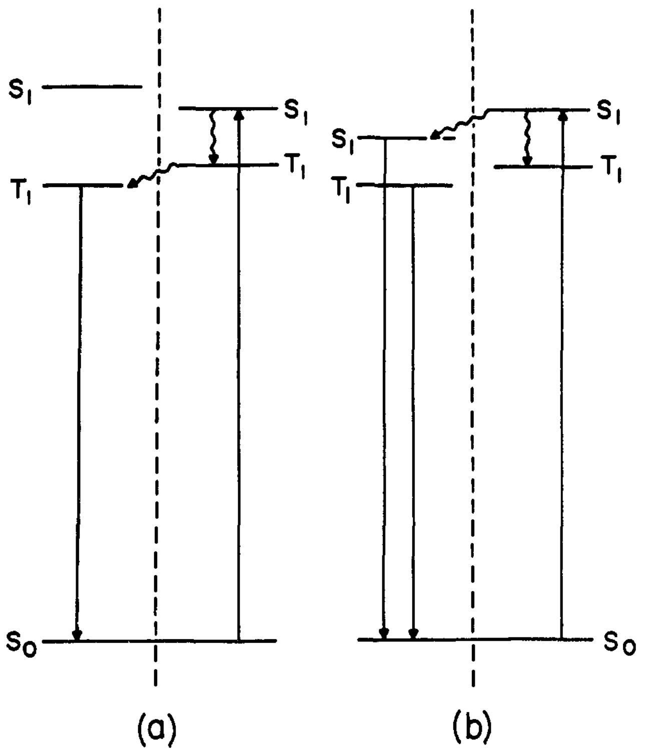


Figure 7.—Energy level schemes for mixed-crystal emission experiments. In each case, guest levels are shown to the left of the dashed lines. Case a corresponds to naphthalene in benzophenone, while case b represents chrysene as a guest in naphthalene.

emission is observed)—all in a time shorter than 2.6 sec, the normal lifetime of $C_{10}H_8$ phosphorescence. The tunneling process is enhanced at higher temperatures or guest concentrations. No tunneling is observed between the singlet levels of $C_{10}H_8$ and the impurity centers.

Nieman and Robinson (264) have conducted experiments on crystals of benzene-d_6 containing guest impurities of C_6H_5D and C_6H_6. These guest molecules have triplet levels of 170 and 200 cm^{-1}, respectively, below that of C_6D_6, and emission will occur only from the guest molecules at low temperatures. The relative amounts of emission from the two guests should depend on their relative concentrations if guest-to-guest transfer does not occur; this was found to hold for fluorescence emission but not for phosphorescence, where the C_6H_6 was favored 10:1 when each guest concentration was 0.4%. These results are very significant in that they demonstrate a higher migration rate for triplet than for singlet excitation under certain conditions; in this case, transfer can occur through about ten host molecules per triplet lifetime. This means that the interaction responsible for triplet transfer (specifically β, the excitation transfer matrix element for the 0,0 level of the lowest triplet state) is much greater than had been estimated (326), and in fact can be as great as that for singlet transfer. Nieman and Robinson (264) estimate $\beta = 1$ cm^{-1} for crystalline benzene (with 1–50 cm^{-1} being reasonable), while for singlet transfer $\beta = 1\text{–}10^4$. But since triplet radiative lifetimes are much longer, *the degree of excitation transfer per lifetime (efficiency of transfer) should be greater for triplets than for singlets by a factor of 10^4–10^8.*

The high efficiency of triplet migration in the naphthalene–benzophenone system has been emphasized by the work of Hochstrasser (147); phosphorescence is exclusively that of naphthalene down to guest concentrations of 10^{-5} mole/mole, an order-of-magnitude below the limiting concentrations usually practical in analogous experiments on singlet energy transfer. The phosphorescence intensity is independent of temperature between 77 and 300°K, in spite of the 100-fold decrease in the phosphorescence intensity (and presumably, the triplet lifetime) of a pure benzophenone crystal on warming to room temperature. If the triplet lifetime of benzophenone is reduced from 10^{-2} to 10^{-4} sec on warming, and only one molecule in 10^5 (the guest) can emit, then the unchanged phosphorescence intensity indicates a triplet migration rate of at least 10^9 sec^{-1}; other experimental results suggest an even higher figure of 10^{10} sec^{-1} (147). Similar lack of temperature effect was noted in other work in which chrysene, pyrene, and anthracene served as guests (152). Although the fluorescence origins of these molecules lie below the excited singlet state of benzophenone, no fluorescence was observed from these crystals (155); this must be a consequence of the rapid rate($\sim 10^{10}$ sec^{-1}) of intersystem crossing and the high phosphorescence quantum efficiency of benzophenone.

Total emission experiments on mixed crystals corresponding to the scheme of Figure 7b permit comparison of both sensitized fluorescence and phosphorescence from the guest, and thus the relative migration rates of singlet and triplet excitation. For example, the ϕ_P/ϕ_F ratio of 1,2-benzanthracene is only 10^{-3} in EPA (240), but the benzophenone-sensitized ratio is about 1:1 (148). Similarly, Hochstrasser and Hunter (151) noted an increase in the phosphorescence/fluorescence ratio of chrysene (in naphthalene) when the light is absorbed only by the host, compared to the ratio measured by direct excitation of the chrysene in the host lattice. This also shows that the host is not active in "perturbing" the intersystem-crossing process of the guest by some sort of solvent effect.

The facile migration of triplet excitation should lead to frequent "collisions" of triplet excitons at high concentrations, and thus to triplet annihilation and delayed fluorescence in pure crystals and mixed crystals of high guest concentration. These processes are discussed in the next section; it should suffice to mention here that Sternlicht, Nieman, and Robinson (376) predict triplet annihilation to be highly favored (over transfer) in pure hydrocarbon crystals. It is well known that many "pure" organic crystals phosphoresce only feebly if at all; for example, the phosphorescence/fluorescence ratio of triphenylene is reduced to about 2% of its rigid-glass solution value in the crystal (155). Phosphorescence from naphthalene (or β-methylnaphthalene?), phenanthrene, and chrysene (271a) is also very weak. In all these cases there are serious doubts as to whether the emission being observed is really that of the substance under investigation. Sternlicht, Nieman, and Robinson (376) report a rapid fall-off of benzene-h_6 phosphorescence yield and lifetime as its concentration is raised from 1 to 5% in C_6D_6. In highly purified benzene (376) and naphthalene (86) samples, it was not possible to find any phosphorescence identifiable with these molecules.

Although the question "do pure aromatic hydrocarbon crystals phosphoresce?" remains open, there is little doubt that the phosphorescence readily observed in crystals of aromatic *carbonyl* compounds, *e.g.*, benzophenone, benzaldehyde, and fluorenone, is genuine. Besides having short lifetimes, their triplet states are characterized by considerable localization of excitation in the region of the carbonyl group, the remainder of the molecule "insulating" the triplet excitation from interaction with other triplets. The resulting decreased interaction is more of an impediment to triplet annihilation than transfer, and emission can compete more favorably.

3. Excitation with High-Intensity Long Wavelength Sources

Biphotonic excitation of blue fluorescence by red light was first demonstrated in organic crystals by Peticolas, Goldsborough, and Rieckhoff (286), who used a laser as the exciting source. Similar results were obtained by Singh and Stoicheff (364); these authors were unable to detect any measurable S → T absorption in anthracene at the frequency of their laser, and found that the fluorescence followed the laser output spike-for-spike, with no apparent delay. Peticolas and Rieckhoff (287) confirmed the lack of delay in anthracene crystal fluorescence, and reported the same type of emission from solutions of anthracene, phenanthrene, and benzpyrene; in the latter, no dependence of fluorescence lifetime on concentration was noted.

Kepler, Caris, Avakian, and Abramson (197) had also detected fluorescence from crystalline anthracene upon laser excitation, and later by use of red light from a xenon arc lamp (8), but their results indicated that excitation occurs by direct S → T absorption in anthracene, followed by triplet–triplet annihilation and delayed fluorescence, and in fact they measured the S → T excitation spectrum of anthracene by varying the wavelength of the red light. In the laser experiment, their oscillogram clearly shows that about 10% of the fluorescent light is emitted after the laser pulse has ceased. From these experiments, and more recent ones by others (138, 402), it appears that excitation with red light can produce both direct one-photon excitation to the triplet state (resulting in triplet–triplet annihilation and delayed fluorescence) and double-photon absorption to a singlet-excited state (followed by normal fluorescence); the tandem triplet–photon process, in which one triplet-excited molecule absorbs another photon, has been shown to be negligible in crystalline anthracene and naphthalene (402). Stoicheff and co-workers (363) and Silver and Zahlen (360) have shown that double-photon absorption to the singlet-excited state can also be followed by intersystem crossing and production of a triplet exciton; two of these then interact to create a new excited singlet, resulting in delayed fluorescence having a *fourth-power* dependence on excitation intensity.

A comprehensive review and discussion of laser-generated excitation in anthracene crystals has recently been given (363) in which are reported the results of numerous experiments on the effects of excitation intensity and wavelength, temperature, and crystal purity on the normal and delayed fluorescence. They propose that double-photon absorption is to a high vibronic level of the ^1L_a ($^1B_{2u}$) state of anthracene, rather than to a (probably nonexistent) electronic state of ^1A_g symmetry as was originally suggested. Their laser frequency was 350 cm^{-1} below the S → T absorption frequency, and hence the I^2-dependent delayed fluorescence (which predominates at low exciting intensities where two-photon absorption is less important) shows an activation energy of this amount. They made the very interesting observation that delayed fluorescence excited by the second harmonic of the laser (corresponding to direct excitation of the ^1L_a band of anthracene) exhibits an activation energy of twice this amount, suggesting that the "reverse annihilation" process of one excited singlet creating two triplet excitons is occurring.

A very important question that has not been satisfactorily answered is this: If triplet exciton migration is a rapid and efficient process, then why should T–T annihilative fluorescence be delayed at all? Sternlicht, Nieman, and Robinson (377) suggest that triplet annihilation in very pure or very impure crystals should result in rapid fluorescence proportional to the *first* power of the excitation intensity, rather than to the square. They suggest that I^2-dependent delayed fluorescence, when it is observed, is probably due to a low concentration of impurity in the crystal being involved in the emission process. The authors thus conclude (377) that T–T annihilation in "real pure" crystals should not be delayed. This is contrary to theoretical calculations (173) which, by using diffusion-controlled migration of triplet excitons, the diffusion length, rate constant of interaction as well as band width of triplet excitons are predicted and found to be in excellent agreement with observations. Further experimental research in this area might be very fruitful.

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