

Theo yêu cầu của khách hàng, trong một năm qua, chúng tôi đã dịch qua 16 môn học, 34 cuốn sách, 43 bài báo, 5 sổ tay (chưa tính các tài liệu từ năm 2010 trở về trước) Xem ở đây

**DỊCH VỤ  
DỊCH  
TIẾNG  
ANH  
CHUYÊN  
NGÀNH  
NHANH  
NHẤT VÀ  
CHÍNH  
XÁC  
NHẤT**

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significantly greater than those encountered in absorption methods.

Lớn hơn đáng kể so với những giá trị thường gặp trong các phương pháp hấp

Finally, the selectivity of luminescence procedures is often better than that of absorption methods. Luminescence methods, however, are much less widely applicable than absorption methods because of the relatively limited number of chemical systems that can be made to produce luminescence.

9A

### THEORY OF FLUORESCENCE AND PHOSPHORESCENCE

Fluorescence occurs in simple as well as in complex gaseous, liquid, and solid chemical systems. The simplest kind of fluorescence is that exhibited by dilute atomic vapors. For example, the 3s electrons of vaporized sodium atoms can be excited to the 3p state by absorption of radiation of wavelengths 5896 and 5890 Å. After  $10^{-5}$  to  $10^{-8}$  s, the electrons return to the ground state and in so doing emit radiation of the same two wavelengths in all directions. This type of fluorescence, in which the absorbed radiation is reemitted without a change in frequency, is known as resonance radiation or resonance fluorescence.

Molecular species also exhibit resonance fluorescence on occasion. Much more often, however, molecular fluorescence (or phosphorescence) bands are found centered at wavelengths that are longer than the resonance line. This shift toward longer wavelengths is termed the Stokes shift.

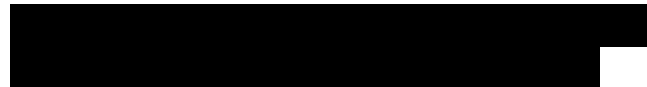
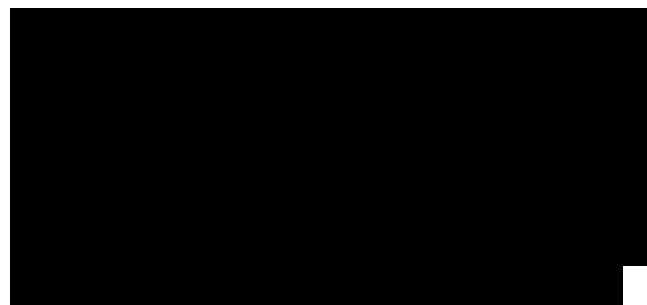
9A-1 Excited States Producing Fluorescence and Phosphorescence

thụ. Cuối cùng, tính chọn lọc của các quá trình phát quang thường tốt hơn của các phương pháp hấp thụ. Tuy nhiên, khả năng ứng dụng của các phương pháp phát quang thấp hơn nhiều so với các phương pháp hấp thụ do số lượng hệ vật chất có thể phát quang có giới hạn.

checked

### LÝ THUYẾT VỀ HUỖNH QUANG VÀ LÂN QUANG

Hiệu ứng huỳnh quang xuất hiện trong những hệ hóa học rắn, lỏng, khí đơn giản cũng như phức tạp. Loại hiệu ứng huỳnh quang đơn giản nhất xuất hiện trong hơi nguyên tử loãng. Chẳng hạn, các electron 3s của đám hơi nguyên tử natri có thể được kích thích đến trạng thái 3p thông qua hấp thụ các bước sóng 5896 và 5890 Å. Sau  $10^{-5}$  đến  $10^{-8}$  s, các electron trở về trạng thái cơ bản và trong quá trình như thế sẽ phát ra hai bước sóng như các bước sóng hấp thụ theo tất cả các hướng. Loại hiệu ứng huỳnh quang trong đó bức xạ hấp thụ được tái phát xạ mà không có sự thay đổi tần số được gọi là bức xạ cộng hưởng hoặc huỳnh quang cộng hưởng.



The characteristics of fluorescence and phosphorescence spectra can be rationalized by means of the simple molecular orbital considerations described in Section 8B-1. However, an understanding of the difference between the two photoluminescence phenomena

requires a review of *electron spin and single excited states*.

### ELECTRON SPIN

The Pauli exclusion principle states that no two electrons in an atom can have the same set of four quantum numbers. This restriction requires that no more than two electrons can fit in an orbital; furthermore, the two must have opposed spin states. Under this circumstance, the spins are said to be paired. Because of spin pairing, most molecules have no net magnetic field and are thus said to be diamagnetic—that is, they are repelled by permanent magnetic fields. In contrast, free radicals, which contain an unpaired electron, have a magnetic moment and consequently are attracted into a magnetic field; free radicals are thus said to be paramagnetic.

### SINGLET/TRIPLET EXCITED STATES

A molecular electronic state in which all electron spins are paired is called a singlet state, and no splitting of energy level occurs when the molecule is exposed to a magnetic field (here, we neglect the effects of nuclear spin). The ground state for a free radical, on the

other hand, is a doublet state, because the odd electron can assume two orientations in a magnetic field, which imparts slightly different energies to the system."

When one of a pair of electrons of a molecule is excited to a higher energy level, a singlet or a triplet state is permitted. In the excited singlet state, the spin of the promoted electron is still paired with the ground-state electron; in the triplet state, however, the spins of the two electrons have become unpaired and are thus parallel. These states can be represented as follows, where the arrows represent the direction of spin.

The nomenclature of singlet, doublet, and triplet derives from spectroscopic *multiplicity* considerations, which

**need not concern us here.** Note that the excited triplet state is less energetic than the corresponding excited singlet state.

The properties of a molecule in the excited triplet state differ significantly from those of the excited singlet state. For example, a molecule is paramagnetic in the former and diamagnetic in the latter. More important, however, is the fact that a singlet/triplet transition (or the reverse), which also involves a change in electronic state, is a significantly less probable event than the corresponding singlet/singlet transition. As a consequence, the average lifetime of an excited triplet state may range from  $10^{-4}$  to several seconds, as compared with an average lifetime of  $10^{-5}$  to  $10^{-8}$  s for an excited singlet state.

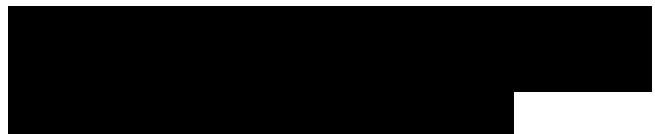
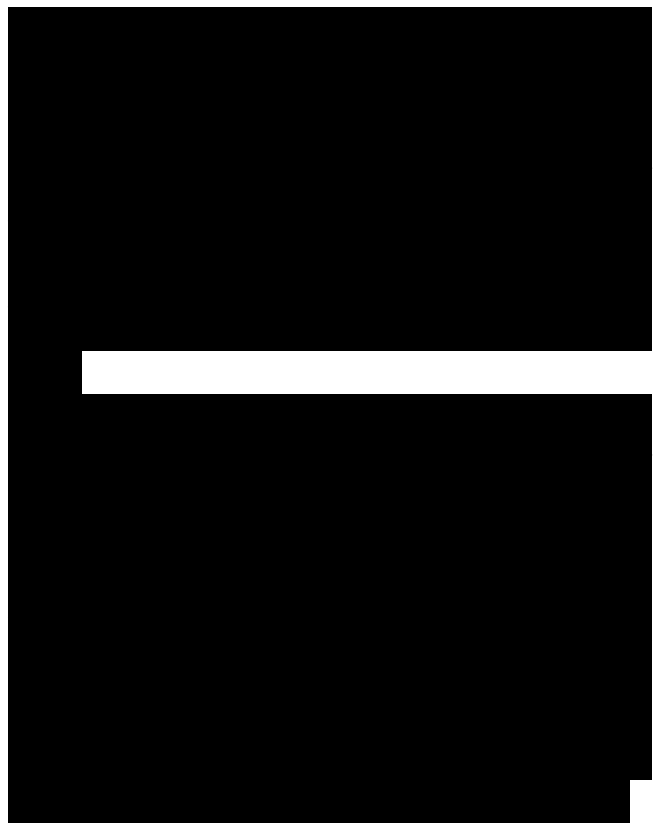
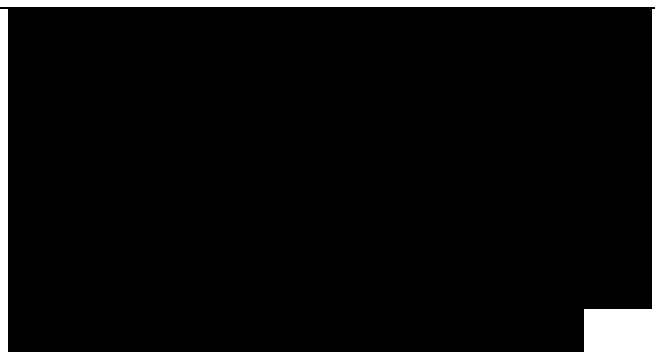
Furthermore, radiation-induced excitation of a ground-state molecule to an excited triplet state has a low probability of occurring, and absorption peaks due to this process are several orders of magnitude less intense than the analogous singlet/singlet transition. We shall see, however, that an excited triplet state can be populated from an excited singlet state of certain molecules; the ultimate consequence of this process is often phosphorescence.

#### ENERGY LEVEL DIAGRAMS FOR PHOTOLUMINESCENT MOLECULES

Figure 9-1 is a partial energy level diagram for a typical photoluminescent molecule. The lowest heavy horizontal line represents the ground-state energy of the molecule, which is normally a singlet state and is labeled  $S_0$ . At room temperature, this state represents the energies of essentially all of the molecules in a solution.

The upper heavy lines are energy levels for the ground vibrational states of three excited electronic states. The two lines on the left represent the first ( $S_1$ ) and second ( $S_2$ ) electronic singlet states. The one on the right ( $T_1$ ) represents the energy of the first electronic triplet state. As is normally the case, the energy of the first excited triplet state is lower than the energy of the corresponding singlet state.\*

Numerous vibrational energy levels are associated with each of the four electronic states, as suggested by the lighter horizontal lines.



As shown in Figure 9-1, excitation of this molecule can be brought about by absorption of two bands of radiation, one centered about the wavelength  $\lambda_1$  and the second around the shorter wavelength  $\lambda_2$ . Now that the excitation process results in conversion of the molecule to one of the several excited vibrational states. Note also that direct excitation to the triplet state is not shown. This transition does not occur to any significant extent, because this process involves a change in multiplicity, an event that, as we have mentioned, has a low probability of occurrence (a transition of this type is sometimes called forbidden).

#### 9A-2 Rates of Absorption and Emission

The rate at which a photon of radiation is absorbed is enormous, the process requiring on the order of  $10^{-14}$  to  $10^{-15}$  s. Fluorescent emission, on the other hand, occurs at a significantly slower rate. Here, lifetime of the excited state is inversely related to the molar absorptivity of the absorption peak corresponding to the excitation process. Thus, for molar absorptivities in the  $10^3$  to  $10^5$  range, lifetimes of excited states are  $10^{-7}$  to  $10^{-8}$  s. For weakly absorbing systems, where the probability of the transition process is smaller, lifetimes may be as long as  $10^{-5}$  to  $10^{-6}$  s. As we have noted, the average rate for a triplet to singlet transition is less than that of a corresponding singlet to singlet transition. Thus, phosphorescent

emission requires times in the range of  $10^{-4}$  to 10 s or more.

#### • 9A-3 Deactivation Processes

An excited molecule can return to its ground state by a combination of several mechanistic steps. As shown by the straight vertical arrows in Figure 9-1, two of these steps, fluorescence and phosphorescence, involve the release of a photon of radiation. The other deactivation steps, indicated by wavy arrows, are radiationless processes. The favored route to the ground state is the one that minimizes the lifetime of the excited state. Thus, if deactivation by fluorescence is rapid with respect to the radiationless processes, such emission is observed. On the other hand, if a radiationless path has a more favorable rate constant, fluorescence is either absent or less intense.

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Photoluminescence is limited to a relatively small number of systems incorporating structural and environmental features that cause the rate of radiationless relaxation or deactivation processes to be slowed to a point where the emission reaction can compete kinetically. Information concerning emission processes is sufficiently complete to permit a quantitative accounting of their rates. Understanding of other deactivation routes, however, is rudimentary at best; for these processes, only qualitative statements or speculations about rates and mechanism can be put forth.

Nevertheless, the interpretation of photoluminescence requires consideration of these other routes.

#### VIBRATIONAL RELAXATION

As shown in Figure 9-1, a molecule may be promoted to any of several vibrational levels during the electronic excitation process. In solution, however, the excess vibrational energy is immediately lost as a consequence of collisions between the molecules of the excited species and those of the solvent; the result is an energy transfer and a minuscule increase in temperature of the solvent. This relaxation process is so efficient that the average lifetime of a vibrationally excited molecule is  $10^{-12}$  s or less, a period significantly shorter than the average lifetime of an electronically excited state. As a consequence, fluorescence from solution, when it occurs, always involves a transition from the lowest vibrational level of an excited electronic state. Several closely spaced peaks are produced, however, because the electron can return to any one of the vibrational levels of the ground state (Figure 9-1), whereupon it will rapidly fall to the lowest ground state by further vibrational relaxation.

A consequence of the efficiency of vibrational relaxation is that the fluorescence band for a given electronic transition is displaced toward lower frequencies or longer wavelengths from the absorption band (the Stokes shift); overlap occurs only for the resonance peak involving transitions between the lowest



vibrational level of the ground state and the corresponding level of the excited state.

### INTERNAL CONVERSION

The term internal conversion describes intermolecular processes by which a molecule passes to a lower-energy electronic state without emission of radiation. These processes are neither well defined nor well understood, but it is apparent that they are often highly efficient, because relatively few compounds exhibit fluorescence.

Internal conversion appears to be particularly efficient when two electronic energy levels are sufficiently close for there to be an overlap in vibrational energy levels. This situation is depicted for the two excited singlet states in Figure 9-1. At the overlaps shown, the potential energies of the two excited states are identical; this equality apparently permits an efficient transition. Internal conversion through overlapping vibrational levels is usually more probable than the loss of energy by fluorescence from a higher excited state. Thus, referring again to Figure 9-1, excitation by radiation of  $X_2$  usually produces fluorescence of wavelength  $X_3$  to the exclusion of a band that would result from a transition between  $S_a$  and  $S_Q$ . Here the excited molecule proceeds from the higher electronic state to the lowest vibrational state of the lower electronic excited state via a series of vibrational relaxations, an internal conversion, and then further relaxations. Under these circumstances, the fluorescence occurs at  $A_j$  only,

regardless of whether radiation of wavelength  $\lambda$  or  $X_2$  was responsible for the excitation. Quinine provides a classical example of this type of behavior (see Problem 9-11); this naturally occurring substance possesses two analytically useful excitation bands, one centered at 250 nm and the other at 350 nm. Regardless of which wavelength is used to excite the molecule, however, the wavelength of maximum emission is 450 nm.

The mechanisms of the internal conversion process  $S_1 \rightarrow S_0$  shown in Figure 9-1 are not well understood. The vibrational levels of the ground state may overlap those of the first excited electronic state; under such circumstances, deactivation will occur rapidly by the mechanism just described. This situation prevails with aliphatic compounds, for example, and accounts for the fact that these species seldom fluoresce; in this class of compounds, deactivation by energy transfer through overlapping vibrational levels occurs so rapidly that fluorescence does not have time to occur.

Internal conversion may also result in the phenomenon of predissociation. Here, the electron moves from a higher electronic state to an upper vibrational level of a lower electronic state in which the vibrational energy is great enough to cause rupture of a bond. In a large molecule, there is an appreciable probability for the existence of bonds with strengths less than the electronic excitation energy of the chromophores.

Rupture of these bonds can occur as a consequence of absorption by the chromophore followed by internal conversion of the electronic energy to vibrational energy associated with the weak bond.

Predissociation should be differentiated from dissociation, in which the absorbed radiation excites the electron of a chromophore directly to a sufficiently high vibrational level to cause rupture of the chromophoric bond; no internal conversion is involved. Dissociation processes also compete with the fluorescent process. |

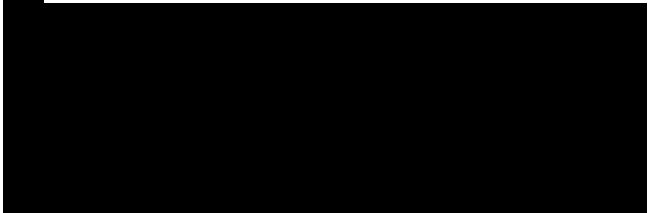
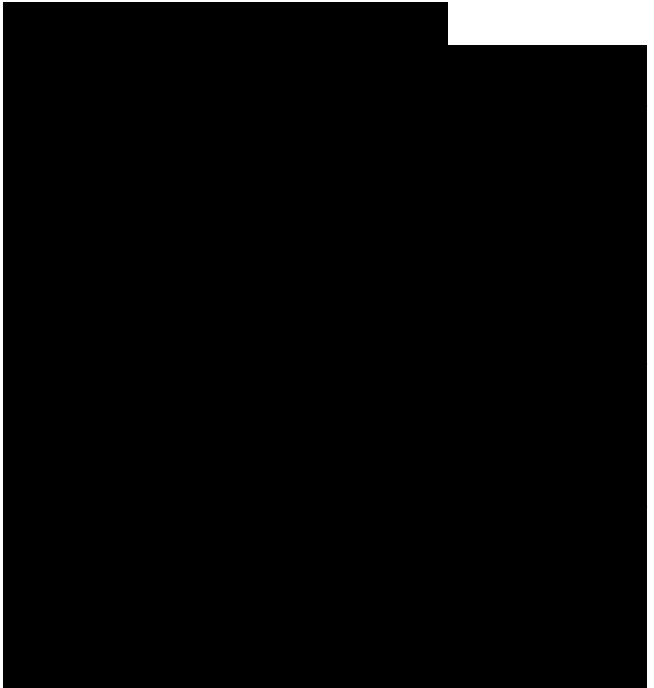
#### EXTERNAL CONVERSION

Deactivation of an excited electronic state may involve interaction and energy transfer between the excited molecule and the solvent or other solutes. These processes are called external conversions. Evidence for external conversion includes the marked effect upon fluorescence intensity exerted by the solvent; furthermore, those conditions that tend to reduce the number of collisions between particles (low temperature and high viscosity) generally lead to enhanced fluorescence. The details of external conversion processes are not well understood.

Radiationless transitions to the ground state from the lowest excited singlet and triplet states (Figure 9-1) probably involve external conversions as well as internal conversions.

#### INTERSYSTEM CROSSING

Intersystem crossing is a process -in



which the spin of an excited electron is reversed and a change in multiplicity of the molecule results. As with internal conversion, the probability of this transition is enhanced if the vibrational levels of the two states overlap. The singlet/triplet transition shown in Figure 9-1 is an example; here, the lowest singlet vibrational state overlaps one of the upper triplet vibrational levels, and a change in spin state is thus more probable.

Intersystem crossings are most common in molecules that contain heavy atoms, such as iodine or bromine (the heavy-atom effect). Apparently spin/orbital interactions become large in the presence of such atoms, and a change in spin is thus more favorable. The presence of paramagnetic species such as molecular oxygen in solution also enhances intersystem crossing and consequently decreases fluorescence.

#### PHOSPHORESCENCE

Deactivation may also involve phosphorescence. After intersystem crossing to an excited triplet state, further deactivation can occur either by internal or external conversion or by phosphorescence. A triplet/singlet transition is much less probable than a singlet/singlet conversion; as has been noted, the average lifetime of the excited triplet state with respect to emission ranges from  $10^{-4}$  to 10 or more. Thus, emission from such a transition may persist for some time after irradiation has been discontinued.

External and internal conversions compete so successfully with phosphorescence that this kind of emission is ordinarily observed only at low temperatures, in highly viscous media, or by molecules that are adsorbed on solid surfaces.

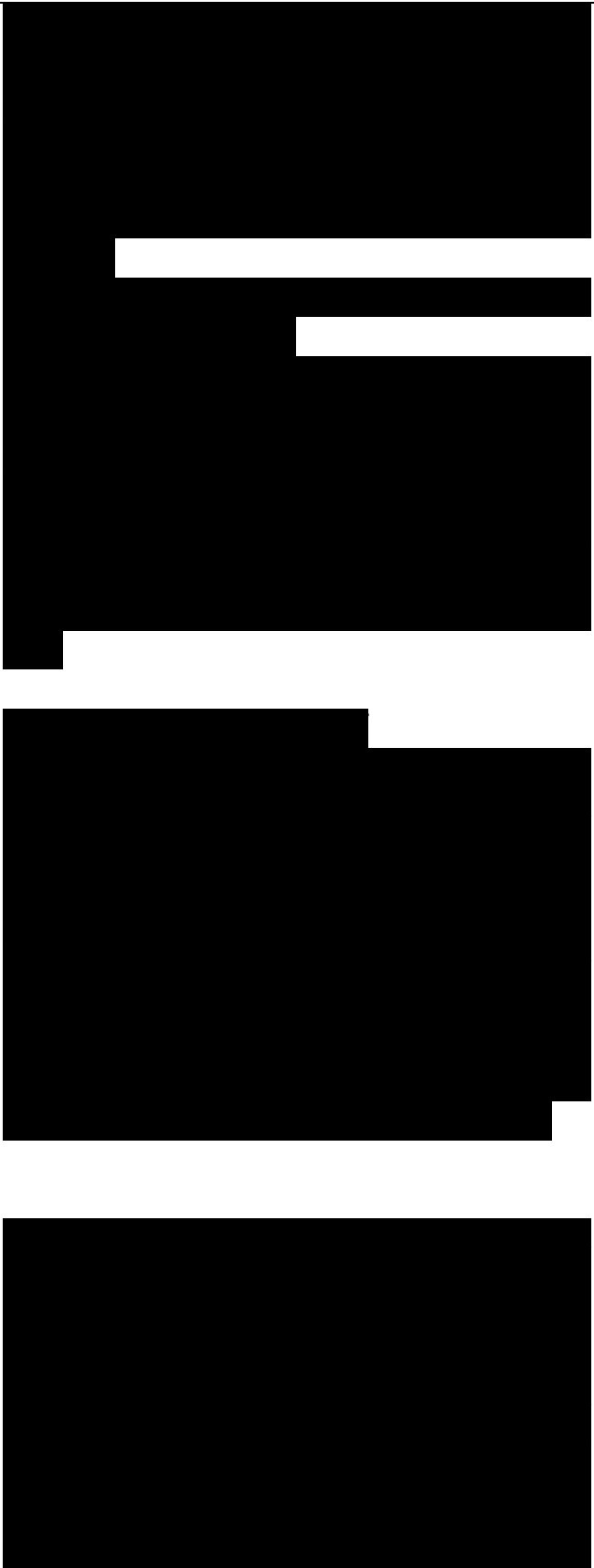
#### 9A—4 Variables That Affect Fluorescence and Phosphorescence

Both molecular structure and chemical environment are influential in determining whether a substance will or will not fluoresce (or phosphoresce); these factors also determine the intensity of emission when photoluminescence does occur. The effects of some of these variables are considered briefly in this section.

#### QUANTUM YIELD

The quantum yield, or quantum efficiency, for fluorescence or phosphorescence is simply the ratio of the number of molecules that luminesce to the total number of excited molecules. For a highly fluorescent molecule such as fluorescein, the quantum efficiency under some conditions approaches unity. Chemical species that do not fluoresce appreciably have efficiencies that approach zero.

From a consideration of Figure 9-1 and our discussion of deactivation processes, it is apparent that the fluorescence quantum yield  $\phi_f$  for a compound must be determined by the relative rate constants  $k_x$  for the processes by which the lowest excited singlet state is de-activated—namely, fluorescence ( $k_f$ ), intersystem crossing



( $k_{ci}$ ), external conversion ( $k_{ec}$ ), internal conversion ( $k_{ic}$ ), predissociation ( $k^*$ ), and dissociation ( $k_d$ ). We may express these relationships by the equation

$$\langle J \rangle = \frac{k_f + k_{ic} + k_{pd} + k_d}{k_f + k_{ic} + k_{ec} + k_{ci} + k^* + k_d} \quad (9-1)$$

where the  $k$  terms are the respective rate constants for the several processes enumerated above.

Equation 9-1 permits a qualitative interpretation of many of the structural and environmental factors that influence fluorescent intensity. Those variables that lead to high values for the fluorescence rate constant  $k_f$  and low values for the other  $k$  terms enhance fluorescence. The magnitude of  $k_f$ , the predissociation rate constant  $k^*$ , and the dissociation rate constant  $k_d$  are mainly dependent upon chemical structure; the remaining constants are strongly influenced by environment and to a somewhat lesser extent by structure.

**TRANSITION TYPES IN FLUORESCENCE** It is important to note that fluorescence seldom results from absorption of ultraviolet radiation of wavelengths lower than 250 nm, because such radiation is sufficiently energetic to cause deactivation of the excited states by predissociation or dissociation. For example, 200-nm radiation corresponds to about  $600 \text{ kJ/mol}$ ; most molecules have at least some bonds that can be ruptured by energies of this magnitude. As a consequence, fluorescence due to  $\pi \rightarrow \pi^*$  transitions is seldom observed; instead, such emission is confined to

the less energetic  $it^* \rightarrow IT$  and  $ir^* \rightarrow$   $n$  processes (see Figure 8-3, page 152, for the relative energies associated with these transitions).

As we have noted, an electronically excited molecule ordinarily returns to its lowest excited state by a series of rapid vibrational relaxations and internal conversions that produce no emission of radiation. Thus, fluorescence most commonly arises from a transition from the first excited electronic state to one of the vibrational levels of the electronic ground state. For the majority of fluorescent compounds then, radiation is produced by either an  $n, \rightarrow r^*$  or a  $ir, ir^*$  transition, depending upon which of these is the less energetic.

**QUANTUM EFFICIENCY AND TRANSITION TYPE** It is observed empirically that fluorescent behavior is more commonly found in compounds in which the lowest energy transition is of a  $ir, ir^*$  type than in compounds in which the lowest energy transition is of the  $n, it^*$  type; that is, the quantum efficiency is greater for  $it^* \rightarrow$   $it$  transitions.

The greater quantum efficiency associated with the state can be rationalized in two ways. First, the molar absorptivity of a  $TT \rightarrow it^*$  transition is ordinarily 100- to 1000-fold greater than for an  $n \rightarrow it^*$  process, and this quantity represents a measure of transition probability in either direction. Thus, the inherent lifetime associated with a  $u \rightarrow it^*$  transition is shorter ( $10^{-7}$  to  $10^{-9}$  s

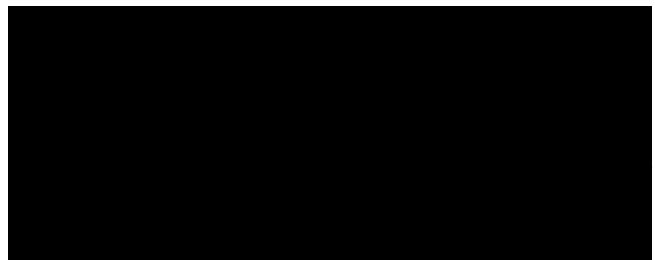
compared with  $10^{-5}$  to  $10^{-7}$  s for an  $n, \pi^*$  transition) and  $k_{\text{IC}}$  in Equation 9-1 is larger.

It is also believed that the rate constant for intersystem crossing  $k_{\text{ISC}}$  is smaller for  $\pi, \pi^*$  transitions, because the energy difference between the singlet/triplet states is larger; that is, more energy is required to unpair the electrons of the  $\pi^*$  excited state. As a consequence, overlap of triplet vibrational levels with those of the singlet state is less, and the probability of an intersystem crossing is smaller.

In summary, then, fluorescence is more commonly associated with  $\pi, \pi^*$  transitions because such transitions exhibit shorter average lifetimes ( $\tau$ , is larger) and because the deactivation processes that compete with fluorescence are less likely to occur.

**FLUORESCENCE AND STRUCTURE** The most intense and the most useful fluorescence is found in compounds containing aromatic functional groups with low-energy  $\pi, \pi^*$  transition levels. Compounds containing aliphatic and alicyclic carbonyl structures or highly conjugated double-bond structures may also exhibit fluorescence, but the number of these is small compared with the number in the aromatic systems.

Most unsubstituted aromatic hydrocarbons fluoresce in solution, the quantum efficiency usually increasing with the number of rings and their degree of condensation. The simple heterocyclics, such as pyridine, furan,





thiophene, and pyrrole, do not exhibit fluorescence: on the other hand, fused-ring structures ordinarily do. With nitrogen heterocyclics, the lowest-energy electronic transition is believed to involve an  $n \rightarrow \pi^*$  system that rapidly converts to the triplet state and prevents fluorescence. Fusion of benzene rings to a heterocyclic nucleus, however, results in an increase in the molar absorptivity of the absorption peak. The lifetime of an excited state is shorter in such structures; fluorescence is thus observed for compounds such as quinoline, isoquinoline, and indole.

Substitution on the benzene ring causes shifts in the wavelength of absorption maxima and corresponding changes in the fluorescence peaks. In addition, substitution frequently affects the fluorescence efficiency: some of these effects are illustrated by the data for benzene derivatives in Table 9-1.

The influence of halogen substitution is striking; the decrease in fluorescence with increasing atomic number of the halogen is thought to be due in part to the heavy atom effect, which increases the probability for intersystem crossing to the triplet state. Predissociation is thought to play an important role in iodo- benzene and in nitro derivatives as well; these compounds have easily ruptured bonds that can absorb the excitation energy following internal conversion.

Substitution of a carboxylic acid or carbonyl group on an aromatic ring generally inhibits fluorescence. In these

compounds, the energy of the  $n, v^*$  transition is less than that of the  $\pi, \pi^*$  transition; as we have pointed out earlier, the fluorescence yield from the former type of system is ordinarily low.

#### EFFECT OF STRUCTURAL RIGIDITY

It is found empirically that fluorescence is particularly favored in molecules that possess rigid structures. For example, the quantum efficiencies for fluorene and biphenyl are nearly 1.0 and 0.2, respectively, under similar conditions of measurement. The difference in behavior appears to be largely a result of the increased rigidity furnished by the bridging methylene group in fluorene. Many similar examples can be cited. In addition, enhanced emission frequently results when fluorescing dyes are adsorbed on a solid surface; here again the added rigidity provided by the solid surface may account for the observed effect.

#### EFFECT OF pH ON FLUORESCENCE

The fluorescence of an aromatic compound with acidic or basic ring substituents is usually pH-dependent. Both the wavelength and the emission intensity are likely to be different for the ionized and nonionized forms of the compound. The data for phenol and aniline shown in Table 9-1 illustrate this effect. The changes in emission of compounds of this type arise from the differing number of resonance species that are associated with the acidic and basic forms of the molecules. For example, aniline has several resonance forms while anilinum has but one. That is,



The additional resonance forms lead to a more stable first excited state; fluorescence in the ultraviolet region is the consequence.

The fluorescence of certain compounds as a function of pH has been used for the detection of end points in acid/base titrations. For example, fluorescence of the phenolic form of 1-naphthol-4-sulfonic acid is not detectable by the eye because it occurs in the ultraviolet region. When the compound is converted to the phenolate ion by the addition of a base, however, the emission peak shifts to visible wavelengths where it can readily be seen. It is of interest that this change occurs at a different pH than would be predicted from the acid dissociation constant for the compound. The explanation of this discrepancy is that the acid dissociation constant for the excited molecule differs from that for the same species in its ground state. Changes in acid or base dissociation constants with excitation are common and are occasionally as large as four or five orders of magnitude.

It is clear from these observations that analytical procedures based on fluorescence frequently require close control of pH.

#### EFFECT OF DISSOLVED OXYGEN

The presence of dissolved oxygen often reduce\* the intensity of fluorescence in a solution. This effect may be the result of a photochemically induced oxidation of the fluorescing species. More commonly, however, the quenching takes place as a

consequence of the paramagnetic properties of molecular oxygen, which promotes intersystem crossing and conversion of excited molecules to the triplet state. Other paramagnetic species also tend to quench fluorescence.

#### EFFECT OF CONCENTRATION ON FLUORESCENT INTENSITY

The power of fluorescent radiation  $F$  is proportional to the radiant power of the excitation beam that is absorbed by the system. That is,

where  $P_0$  is the power of the beam incident upon the solution and  $P$  is its power after traversing a length  $b$  of the medium. The constant  $K'$  depends upon the quantum efficiency of the fluorescent process. In order to relate  $F$  to the concentration  $I$  of the fluorescing particle, we write Beer's law in the form

where  $e$  is the molar absorptivity of the fluorescing molecules and  $ebc$  is the absorbance  $A$ . By substitution of Equation 9-3 into Equation 9-2, we obtain

The exponential term in Equation 9-4 can be expanded as a Maclaurin series to

Provided  $2.303ebc < 0.05$ , of the subsequent terms in the brackets become small with respect to the first; under these conditions, the maximum relative error in

Equation 9-5 caused by dropping all but the first term is 2.5%. Thus, we may write

$$F \ll K'PQ 2.303tbc \quad (9-6)$$

or at constant  $P_0$ ,

$F \gg Kc$  (9-7)

Thus, a plot of the fluorescent power of a solution versus concentration of the emitting species should be linear at low concentrations. When  $c$  becomes great enough so that 2.303 times the absorbance is larger than about 0.05, the higher-order terms in Equation 9-5 become important and linearity is lost;  $F$  then lies below an extrapolation of the straight-line plot.

Two other factors, also responsible for negative departures from linearity at high concentration, are self-quenching and self-absorption. The former is the result of collisions between excited molecules. Radiationless transfer of energy occurs, perhaps in a fashion analogous to the transfer to solvent molecules that occurs in an external conversion. Self-quenching can be expected to increase with concentration because of the greater probability of collisions occurring.

Self-absorption occurs when the wavelength of emission overlaps an absorption peak; fluorescence is then decreased as the emitted beam traverses the solution. The effects of these phenomena are such that a plot relating fluorescent power to concentration may exhibit a maximum.

#### 9A-5 Emission and Excitation Spectra

Figure 9-2 shows three types of photoluminescence spectra for phenanthrene. An excitation spectrum is obtained by measuring luminescence intensity at a fixed wavelength while the excitation wavelength is varied. Fluorescence and phosphorescence

spectra, on the other hand, involve excitation at a fixed wavelength while recording the emission intensity as a function of wave- . length.

As was pointed out earlier, photoluminescence usually occurs at wavelengths that are longer than the excitation wavelength. Furthermore, phosphorescence V bands are generally found at higher wavelengths than fluorescence bands are, because in most instances the excited triplet state is lower in energy than the corresponding singlet state. In fact, the wavelength difference between the two provides a convenient measure of energy difference between triplet and singlet states.

