

RADIATIONLESS TRANSITIONS IN GASES AND LIQUIDS

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CONTENTS

I. Introduction	413
II. Gases	414
A. Atomic Gases	414
1. Degrees of Freedom	414
2. Resonance Radiation	414
3. Energy Transfer	414
4. Theory	415
B. Diatomic Gases	416
1. Degrees of Freedom	416
2. Resonance Radiation and Relaxation	416
3. Experimental Methods	416
4. Theory	417
C. Polyatomic Gases	418
1. Degrees of Freedom	418
2. Resonance and Nonresonant Radiation	418
3. Criteria for Luminescence	418
4. Energy Transfer and Chemical Affinity	419
5. Theory	420
III. Liquids	420
A. General Comments	420
B. The Triplet State and Long-Lived Luminescence	421
1. Phosphorescence	421
2. Experimental Methods: Triplet-Triplet Absorption	422
3. Delayed Fluorescence	422
4. Intersystem Crossing	423
5. Other Triplet-State Phenomena	424
C. Energy Transfer	425
1. Intramolecular Energy Transfer	425
2. Sensitized Fluorescence and Related Phenomena	425
3. Triplet-State Energy Transfer	426
4. Heterogeneous Systems	426
5. Mechanisms of Energy Transfer	427
IV. Discussion of Theories	427
V. Reviews and General Articles	429
VI. The Lifetimes of Excited States	429
A. From the Integrated Absorption	429
B. From the Uncertainty Principle	429
C. From the Observed Decay Scheme	430
D. From a Stern-Volmer Quenching Plot	430
VII. References	430

I. INTRODUCTION

The subject of this review is the fate of the energy acquired by molecular systems on absorption of optical photons. Thermodynamic laws state that excited systems must return to thermal equilibrium. However, the time scale of this return can vary from 10^{-12} sec. to over a billion years. The faster times are common to most substances, while the latter time occurs in green plants which convert the photon energy into chemical energy. Less common are cases where the energy reappears as emitted photons within times between 10^{-9}

and 10 sec. The problem of the fate of this energy is formalized as the study of *radiationless transitions*, the changes of state of molecular systems that occur without the emission or absorption of photons. Here *molecular* refers quite generally to any chemical species of molecular dimensions.

In this review, attention is confined to molecular systems that are *semi-isolated*, which means that a model that considers the excitation as localized is completely valid. Semi-isolated systems are to be distinguished from molecules in aggregates, where the

delocalization of the excitation may play an important role in the radiationless process. To avoid this complication attention is centered on molecular systems in the gas phase at low pressure or in solution—gaseous, liquid, or solid—with suitably inert solvents.

Ironically, radiationless transitions are most often studied by observing the radiation that is emitted. From such observations, one wishes to deduce: (1) the pathway, *i.e.*, the states through which the system passes, and (2) the times involved. Another interesting point is that the quantum state of the system that receives the energy is often ignored. In those cases where the quantum state of the recipient system is considered, the process is called *energy transfer*; if the recipient system is considered as a thermal bath, then the process is called *dissipation*. In liquid solutions, energy transfer generally refers to electronic energy, while transfer of vibrational energy is considered dissipation. In a gas, however, vibrational and even rotational energy transfer are often of distinct interest.

This review presents a survey of gas and liquid experimental studies and theoretical ideas. A vast number of papers related in some way to this topic have appeared, and this review does not represent a complete literature survey of the subject. Experimental observations and particular theoretical explanations have been presented in sections II and III. In section IV some more general theoretical approaches are discussed. General papers on radiationless transitions and some starting points for the study of energy transfer in biological systems are listed in section V. In part VI, different uses of the term “lifetime” and some operational definitions are cited.

II. GASES

The simplest model of a gas is that of hard spheres interacting only in elastic collisions (79, 113). Such a classical model is inadequate for the internal degrees of freedom, which must be treated quantum mechanically. In the present discussion of gases a *semiclassical* model is used, that is, the internal modes are treated quantum mechanically, and the translational modes, classically. In particular, the molecules are considered to follow well-defined trajectories and to engage in two-body collisions. This mixture of classical and quantum pictures can be soundly based on the *correspondence principle* and has been used in other problems (59, 93).

A. ATOMIC GASES

1. Degrees of Freedom

Many basic processes were first studied in atomic gases. Here the only degrees of freedom are translational and electronic, and the atoms exist in well-defined electronic states. Transitions between these states give rise to characteristic series of lines seen in emission and absorption. Excitation may occur di-

rectly to a given excited state of the atom by absorption of a single photon, or, less commonly, by successive absorption of photons. Likewise emission may take place by direct transition to the ground state or in a stepwise manner, as observed in Cs vapor (143).

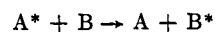
2. Resonance Radiation

When low pressures of an atomic gas are used, one commonly observes *resonance radiation*, direct emission from the primary excited state to the ground state (7, 80, 111, 120, 143). This will occur if the only possible spontaneous transition from the excited state is to the ground state, as is the case for the lowest excited level or for a higher level where intermediate transitions are forbidden. Frequently resonance radiation is used in a wider sense to apply to all emitted radiation from the single initially excited level of an atom or molecule. For an isolated molecule one would expect a quantum yield (photons out per photon in) of unity. Under proper circumstances it is possible to obtain resonance emission from a single hyperfine component of a spectral line.

Two common problems encountered in resonance radiation studies are “imprisoned radiation” and the broadening of spectral lines. The former phenomenon occurs at moderate and high pressures and involves multiple reabsorption and emission of radiation within the volume of the gas. Broadening of spectral lines can be caused by several factors, of which (i) unresolved fine structure, (ii) collisions, (iii) Doppler effect, (iv) Stark broadening, and (v) the finite lifetime of the excited state (*vide infra*) are the most common (93, 111).

3. Energy Transfer

The famous experiments of Franck and Hertz from 1913 to 1916 gave an early demonstration of inelastic collisions on an atomic scale. They found that electrons with less than 4.9 e.v. of energy underwent only elastic collisions with mercury vapor atoms, while at higher kinetic energies the electrons lost considerable energy to the mercury atoms in inelastic collisions. In the latter case there resulted an emission of 2537-Å. light by the mercury vapor. These experiments provided an important confirmation of the existence of stationary states in atoms. Such collisions, in which the kinetic energy of one partner is transformed into internal energy of the other, are designated *collisions of the first kind*. By the principle of microscopic reversibility, reverse processes must also occur. These processes, and all collision processes in which excitation energy is transferred as represented by



(where * designates excitation energy), are called *collisions of the second kind* (63a). One example is the xenon-sensitized dissociation of molecular hydrogen, in which

excited Xe atoms transfer energy to a repulsive excited state of H₂, which very quickly dissociates (24). Another example is the mercury-sensitized decomposition of carbon dioxide (114).

Cario and Franck (26), working in 1923, were probably the first to demonstrate clearly energy transfer between two gas atoms. They illuminated a mixture of mercury and thallium vapors with light absorbed only by the mercury atoms, yet emission of both Hg and Tl lines was observed. When pure thallium vapor was illuminated with the same light, no emission was observed. Clearly the Tl emission resulted from energy transfer from Hg atoms, and it was therefore referred to as "sensitized fluorescence." Sensitized fluorescence has now been observed in many other systems (111).

4. Theory

The study of energy transfer in gases has revealed two general principles that apply to atomic collisions: (1) Energy transfer is most efficient when the least amount of electronic energy is converted into kinetic energy. (2) The total spin of the system is unchanged by the collision.

The first rule is predicted by quantum theory (7, 80, 120) and may be considered as indicating a type of resonance between the states of the collision partners. This is shown schematically in Figure 1, where ΔE appears as an increase in the translational energy of atoms A and B.

The second rule is Wigner's rule of spin conservation (184). It is qualified by the fact that the spin character of atomic and molecular states is not pure. Because of spin-orbit coupling, nominal singlet states have some triple character and *vice versa*. Such nominal singlets and triplets can be roughly expressed as

$$\begin{aligned}\psi_s &= (1 + \lambda^2)^{-1/2}(\Phi_s + \lambda\Phi_T') \\ \psi_T &= (1 + \mu^2)^{-1/2}(\Phi_T + \mu\Phi_s')\end{aligned}$$

where Φ_s and Φ_T are pure singlet and triplet states. Thus the probability of a transition between states of different multiplicity will depend on λ and μ , which are usually small. These parameters increase with atomic number, so that λ is of the order of 10^{-2} for transition metal atoms and may be even larger for heavier atoms.

A scheme for picturing atomic collisions that has proved especially useful is that of potential curve crossings. For this the electronic energy of the two atoms is plotted as a function of internuclear distance, as in Figure 2. Excited states are shown as A* and B*. When the species A* and B collide, there is some probability that the species B* and A will be produced. Such transfers of energy are facilitated if the two potential curves cross.

A unique feature of gas phase systems is that interaction with the environment can be "turned up" by

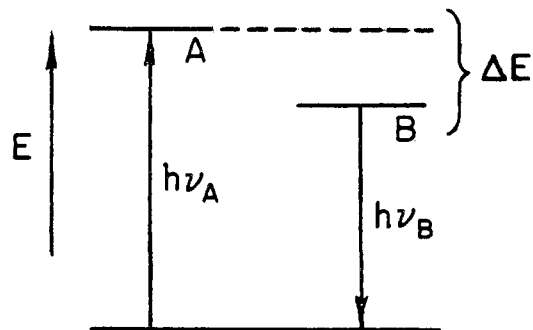


Figure 1.—Energy transfer in collision of species A and B.

increasing the pressure. When a molecule which would otherwise radiate instead transfers its energy in a collision, the result is a quenching of that radiation, and one might think that increasing the pressure should reduce emission intensity. In the classic study of this problem, Stern and Volmer (160) obtained an equation relating the quenching of fluorescence, Q , to the partial pressure of an added foreign gas.

$$Q = \frac{1}{1 + \tau_0 Z_Q}$$

or

$$\frac{1}{Q} = 1 + (\text{constant})P$$

where $Q = I/I_0$ is the ratio of fluorescence intensities with and without foreign gas added, τ_0 is the natural lifetime of the excited atom, Z_Q is the number of effective quenching collisions per second, and P is the pressure.

The limitations of this relation are discussed in ref. 111. Usually only a fraction of all collisions is effective in quenching the emission. Because the quenching depends so strongly on the interaction between the two species, there is no distinct relation between quenching and kinetic cross sections. Also, studies of the polarization of resonance fluorescence show that poor quenchers are generally more efficient in causing depolarization, since they cause collisions which destroy the polarization without dissipating the excitation energy (111).

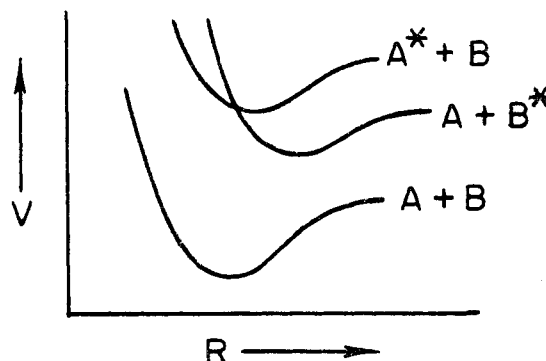


Figure 2.—Potential curves representing the interaction of atoms A and B.

B. DIATOMIC GASES

1. Degrees of Freedom

The presence in diatomic molecules of two types of internal motions, rotations and vibrations, not possible in atoms leads to behavior in diatomic gases which is qualitatively different from that of an atomic gas. The most important change is that the total number of possible states for the system in a given range of energy is very greatly increased. In addition, the possibility of dissociation is now present, and this process may sometimes compete with other processes such as radiative emission and energy transfer. Dissociation may take place directly or by *predissociation*, in which a molecule is excited to a discrete level and undergoes a rapid transition to a level in a continuum of states, causing diffuse bands to occur in the spectrum (see 158).

2. Resonance Radiation and Relaxation

Consider a molecule which has been excited by absorption of a photon to a state with high electronic, vibrational, and rotational energy. The surrounding molecules may be regarded as constituting a thermal bath. Within a limited amount of time the molecule may be expected to reach thermal equilibrium with the surrounding molecules, and its internal energy to have become dissipated into the thermal motion of the assembly; that is to say, it will *relax*. There is no reason to believe that the rotational, vibrational, and electronic internal energies will relax with equal ease—indeed this is not the case, and it may be assumed that the establishment of equilibrium between a given internal mode and the external degrees of freedom proceeds with a relaxation time characteristic of that mode.

Resonance radiation occurs when the diatomic molecule re-emits from the same electronic-vibrational-rotational state into which it was excited. Such radiation can be observed in I_2 (21). It is found that when foreign gas molecules are introduced emissions from other I_2 vibrational and rotational states begin to appear, signifying the transition to nonresonant radiation. A quenching effect on the fluorescence is also observed when the pressure of either the I_2 or the foreign gas is increased (21).

One might reasonably ask why a molecule should not simply lose vibrational and rotational quanta one or a few at a time by emission of infrared photons. This does not occur because the intrinsic rates for such processes are too slow to allow them to compete successfully with other deactivation mechanisms. This follows from the form of the Einstein coefficient for spontaneous emission of radiation between states n and m

$$A_{n \rightarrow m} = \frac{64\pi^4}{3h} \bar{\nu}^3 |\mu_{mn}|^2$$

Here $\bar{\nu}$ is the wave number of the photon emitted, and μ_{mn} is the dipole moment matrix element for the transition. Two factors in this operate against the emission of infrared photons. Firstly, the wave numbers for vibrational transitions are roughly 10 to 100 times smaller than for electronic transitions. Secondly, the dipole moments for vibrational transitions, which can be considered as involving small displacements of the nuclei, are much less than the corresponding electronic dipole moments which involve the more easily displaced electrons.

In only a few cases have purely vibrational emissions from nonequilibrium distributions been observed. Infrared chemiluminescence has been detected in HCl (27) and OH (58). In the latter case it was also possible to show that collisional deactivation proceeded mainly *via* the loss of single vibrational quanta. Very recently Millikan (109) has reported the observation of vibrational resonance fluorescence in CO. This is probably the first such observation in any molecule.

3. Experimental Methods

The study of relaxation kinetics is an active area of investigation at the present time. The experimental details have been discussed by Cottrell and McCoubrey (31) and Jacox and Bauer (78). Methods commonly used involve (1) ultrasonic absorption and dispersion, (2) shock waves, (3) impact tubes, (4) the optical-acoustic effect, and (5) spectroscopic techniques. Of these, ultrasonic procedures have been the most productive, while some of the other methods have not been completely developed.

The velocity of sound in a gas, the parameter used in ultrasonic measurements, is a convenient property to study because it can be related to thermodynamic properties, and it involves a characteristic time, the period of one cycle (31). For an ideal gas

$$V^2 = \left(1 + \frac{R}{C_v}\right) \frac{RT}{M}$$

where V = velocity of sound, C_v = heat capacity, and M = molecular weight. Because the internal modes act essentially independently, one can write

$$C_v = C_{\text{trans}} + C_{\text{vib}} + C_{\text{rot}}$$

The compressions and rarefactions of sound waves may be considered as variations in temperature. If the frequency of the sound is increased it becomes more and more difficult "for the energy to leak from the external into the internal degrees of freedom" (64). As a result, one of the terms in the expression for the heat capacity becomes ineffective and C_v decreases, causing V^2 to increase. If V^2 is plotted against frequency, an inflection point will occur, thus disclosing the relaxation time for a particular mode.

Cottrell and McCoubrey (31) have collected experimental results for a wide variety of diatomic and polyatomic systems. One interesting point is that often the efficiency of vibrational energy transfer is vastly increased with increasing temperature and consequent higher average collision velocities. For example, at room temperature and 1 atm. pressure, O_2 molecules undergo, on the average, 2×10^7 collisions (relaxation time, 3.2×10^{-8} sec.) before losing a quantum of vibrational energy from their $v = 1$ vibrational level. At $3000^\circ K.$, however, one collision generally suffices for vibrational deactivation. By comparison, only about four collisions are necessary for *rotational* deactivation of O_2 at room temperature. In these studies collisional efficiency is generally expressed by Z_{10} , the number of collisions necessary to cause vibrational relaxation from the $v = 1$ vibrational level. Even at its best, *i.e.*, in a moderately large molecule, it takes 50 to 100 collisions to deactivate the lowest vibrational state at room temperature (64). The exchange of vibrational energy between two diatomic species is seen to be most efficient when the vibrational quanta of the two species are closest in energy (25). It is also found that vibrational deactivation in NO, at least, is much more efficient in the excited state than in the ground state (20). Rotational transitions in NO are found to occur at every collision and are not subject to the optical selection rule $\Delta J = \pm 1$ (20).

4. Theory

The first rule governing energy transfer stated previously gives considerable insight into the problem of relaxation in diatomic molecules. Because the energy levels are more closely spaced than in atoms, the possibility of close energy resonance between collision partners is increased. Also, in considering transfer into translational energy, it can be correctly predicted that rotational modes, which have characteristically small quanta ($E_r < kT$), will relax rapidly relative to the relaxation of vibrational modes ($E_v > kT$). Of course, no isolated diatomic molecule can simply transfer energy from one mode into another; conservation rules preclude this. Some interaction is necessary, and there is good reason to believe that binary collisions are ordinarily the main mechanism for such transfer (as opposed, *e.g.*, to collisions with the walls of the container, or radiative transitions) (31).

One way to consider the interaction of two molecules is to represent it in terms of the crossing of potential curves (171), as for atoms. Actually, instead of potential curves, potential hypersurfaces in a higher dimensional space should be considered for the interaction (see 102, 158, 171). However, because of the complications and uncertainties involved, this has not proved useful for quantitative calculations.

The basic quantitative theories of collisional transi-

tion probabilities were developed by Zener (191) and Landau and Teller (92) and have been widely discussed and extended (38, 64, 65, 89, 90, 116, 117, 145, 153a, 155, 176, 177b, 183). Landau and Teller argued that it is important to distinguish between two limiting types of encounters (31, 65, 78, 92, 116, 176).

(1) Adiabatic, or slow collisions. Here the molecule adjusts at all times to the perturbation caused in the collision, and no net energy is transferred.

(2) Nonadiabatic, or fast collisions. In these a part of the molecule is rapidly struck and no adjustment is possible during the short duration of the collision. Such behavior is usually a prerequisite for high-energy transfer efficiency.

It is therefore useful to characterize collisions by a parameter which is the ratio of the effective duration of the collision, T , to the characteristic time, τ , of the internal motion considered. Efficient energy transfer requires $T/\tau < 1$. By estimating T for ordinary gases one can again predict that rotational energy should transfer rather easily in collisions, while vibrational energy should not (31). For example, at room temperature it can be estimated that a collision, considered as a reasonably large interaction between the partners, lasts for roughly 10^{-13} sec. (31). This is very fast compared to typical rotational times of about 10^{-11} sec., but not compared to typical vibrational times of about 10^{-13} sec. Such an analysis neglects any chemical effects in the collision (15, 65). Usually such effects seem not to be very important in diatomics, as Millikan and White (110) have shown, *e.g.*, for O_2 - H_2 collisions. Landau and Teller considered only repulsive forces, which they approximated by an exponential potential. They integrated a transition probability, which depends exponentially on the collision-time parameter above, over a Maxwellian velocity distribution.

The specific form of the interaction potential between collision partners may often be quite important, however (34, 78, 116). It contains contributions not only from electrostatic forces, including multipole terms, but also from induction and dispersion forces. Most commonly the interaction between gas molecules is approximated by the Lennard-Jones 6-12 potential (31, 64)

$$\Phi(r) = 4\epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\}$$

where σ is the intermolecular separation at $\Phi = 0$ and ϵ is the interaction energy when Φ is a minimum. Lennard-Jones constants for many gases have been obtained. However, the Schrödinger equation cannot be solved in closed form using this potential, and other approximate potentials are often used (64).

Present theoretical ideas seem adequate to give reasonable predictions for energy transfer from lower vibrational levels (with low transition probabilities) in diatomic molecules (89). The treatment of transfer

from higher vibrational levels of diatomic molecules and in polyatomic molecules is less well established (15, 21, 188). Calculations show that in low velocity collisions usually one quantum is transferred, but at higher velocities the probability of exchange of several quanta is increased (145).

It should be noted that in most theoretical treatments of collisional energy transfer several simplifying assumptions are made (31). First, internal modes of only one of the collision partners are considered. Second, in almost all cases only the vibrational degrees of freedom are dealt with. Often, only one relative encounter coordinate is used, and one assumes that relative velocities are so large that one can neglect the change in translational energy caused by the inelasticity of the collision. Rotational relaxation is less often studied, although Bird (11) has recently made some interesting comments on this topic, stating that alkali halides, which have large dipole moments, can exchange rotational energy at distances of 50 Å. or more because of their strong dipolar interactions.

C. POLYATOMIC GASES

1. Degrees of Freedom

In what essential features do polyatomic molecules differ from diatomic molecules? Pringsheim (143) and others (102, 162) have discussed this problem. Most apparent is the considerably further increase in the number of possible excited states and the consequently closer spacing of energy levels. For each electronic state in a molecule with n atoms there are now $3n - 6$ ($3n - 5$ in linear molecules) vibrational modes; as a result, zero-point energies can become rather large in larger molecules. Within a given electronic energy level the density of the vibrational states increases rapidly as the energy is increased. For instance, if there are N vibrational modes (consider that they have the same fundamental frequency for simplicity) and if M quanta are available [$E_{\text{vib}} = (M + N/2)h\nu_0$], the number of degenerate states is

$$\frac{(M + N - 1)!}{M!(N - 1)!}$$

In practice, however, these levels may not be equally accessible.

2. Resonance and Nonresonant Radiation

Resonance fluorescence has not been observed in most polyatomic molecules. It is not, however, always absent, as was demonstrated by the early work of Kistiakowsky and co-workers (35, 87). They studied the fluorescence of benzene vapor at pressures from 25 to 0.01 mm. As the pressure was decreased a transition from ordinary high pressure fluorescence, which originates from vibrationally equilibrated levels, to

resonance fluorescence, originating from a definite vibrational level of the excited state, was observed. It was not possible to observe resonance fluorescence from benzene derivatives, even at the lowest pressures.

Parmenter and Kistiakowsky have recently repeated the benzene experiments using photoelectric detection. They found that the quantum yields of the low pressure benzene resonance radiation are higher than those of the high pressure nonresonant radiation (131). In these experiments the benzene is not subject to any dissociative process. Williams and Goldsmith (187) studied naphthacene vapor at very low pressure, exciting with either 2537- or 3650-Å. Hg lines. These lines cause transitions to the second and first excited singlet, respectively. Both excitations give rise to an emission spectrum that is a mirror image of the lowest excited singlet absorption although the higher energy excitation produces a broader spectrum. These observations are similar to earlier ones by Pringsheim on anthracene, and have been interpreted as evidence that internal conversion can occur even in the absence of collisions.

Nonresonant radiation almost inevitably appears either from the lowest excited singlet state or the lowest triplet state (see section III,A). Porter and Wright (141) have reported observations on the triplet states of a number of aromatic vapors. In general, they found triplet lifetimes to be *less* in the vapor than in solution or rigid glass. Furthermore, they reported that intersystem crossing rates appear independent of pressure at the pressures studied.

3. Criteria for Luminescence

It is obvious that much of our information about radiationless transitions in molecules is inferred from information about radiative processes, which are easier to study. For this reason it is important to consider what types of molecules exhibit luminescence. This may appear as fluorescence, defined as an emission between states of like multiplicity, or phosphorescence, an emission between states of unlike multiplicity. General treatments of the subject have been given by Pringsheim (143), Förster (49b), and more recently by Van Duuren (177a).

On the whole, inorganic polyatomic vapors seem not to luminesce, mainly because their absorptions usually lead to dissociation (143). However, most inorganic spectra lie in the far-ultraviolet and are difficult to study, so that there is less information available about them. Pringsheim (143) lists observations of fluorescence only in NO_2 , SO_2 , NH_3 , and H_2O .

Of the organic compounds, saturated hydrocarbons and other aliphatics are usually not fluorescent for much the same reasons as above. Excitation of tightly bound electrons strongly involved in bonding usually leads to dissociation. However, the presence in molecules of certain atoms—such as oxygen, nitrogen, halo-

gens, or metals—often provides conditions favorable for fluorescence (102). Pringhseim has listed 11 fluorescent aliphatic vapors, all of which contain either oxygen or nitrogen.

The vast majority of fluorescent polyatomic molecules are aromatic compounds. In these, electrons which are not so deeply involved in bonding and which have low energy excited states are available for excitation. In heteroaromatics it is found that fluorescence does not usually occur if the lowest singlet level is of the (n, π^*) type, since such a level favors intersystem crossing to the triplet (28, 82, 83). Such a crossing can result in emission from the triplet, or more generally, in an absence of luminescence. No such general effect is found when the lowest singlet is a (π, π^*) state (see section III, B, 1).

4. Energy Transfer and Chemical Affinity

The existence of π -electrons also can have an effect on energy-transfer processes. In an investigation of the quenching of the resonance radiation of sodium, Norrish and Smith (122) found a striking difference in the effectiveness of inert gases and saturated hydrocarbons on the one hand, and unsaturated hydrocarbons on the other. They used the kinetic theory expression for the number of collisions experienced per second

$$Z_Q = 2n\sigma^2 \sqrt{2\pi RT} \left(\frac{1}{M_1} + \frac{1}{M_2} \right)$$

Here n is a number of quenching molecules/cc., M_1 and M_2 are the molecular weights, and σ^2 is the cross section. The unsaturated hydrocarbons showed effective cross sections for the quenching roughly 100 times as large as those of comparable saturated hydrocarbons. The results indicate that energy transfer is more efficient than might be expected from simple kinetic theory considerations. Mori (115) has recently given a quantum mechanical analysis of this topic.

A number of studies of "sensitized luminescence" in polyatomic vapors have been made. Among the most interesting are the investigations of Noyes and his co-workers (72, 73, 124, 132) on energy dissipation in various aldehydes and ketones. One finding of these studies is that the triplet emission of biacetyl can be sensitized by benzene, apparently through a triplet-triplet transfer mechanism. A singlet-singlet transfer can also occur which leads to dissociation of the biacetyl. The results obtained seem to indicate that all conversions to the ground state from the singlets of both biacetyl and benzene occur through the triplet state, and that the triplet states are thereby formed with very high yield. Furthermore, the singlet-triplet crossing rate is independent of collisions at the pressures used, and crossing seems usually to occur from the vibrationally relaxed levels of the lowest singlet. Stevens (163)

has found that benzene can also sensitize the fluorescence of anthracene. Transfer seems to occur with unit efficiency on collision in the gas phase at 170°.

Another interesting phenomenon, first discovered by Neporent (118), is the increase observed in the fluorescence yields of certain highly excited molecules upon the addition of a foreign gas. The molecules involved were excited to a state with an excess of vibrational energy, from which dissociation or crossing to a triplet state could occur. Presumably, if the excess vibrational energy can be removed rapidly by collisions, dissociation (or crossing) does not occur and the molecule is free to fluoresce normally. (An analogous situation with respect to ionization has been described by Platzman (134-136). He states that "superexcited states," which have energies in excess of ionization energy, are of unrecognized importance in radiation chemistry. As described, these states may involve multiple electron excitations, and do not always lead to ionization.)

This so-called "fluorescence stabilization" provides a convenient means for studying the ability of various molecules to carry away vibrational energy in collisions (16, 119, 164). Stevens (164) has found that the average amount of vibrational energy removed per collision from β -naphthylamine by paraffin hydrocarbons increases with the complexity of the added gas, but that the transfer efficiency, as expressed by an accommodation coefficient (which is a measure of the extent of thermal equilibrium the two molecules achieve in the collision), is almost the same for the different molecules. He explains these results by regarding the collisions as quasi-chemical reactions in which an ephemeral "collision complex" is formed. This allows a partial equilibration of vibrational energy to occur.

Bowen and Veljković (18), studying the stabilization of perylene vapor, likewise have noted that stabilizing ability increased with increased molecular weight of the added gas. The reason, they feel, is that heavier molecules allow a longer duration for the collision complex since they move more slowly at a given temperature than do light molecules. Supporting this is the finding that at higher temperatures less energy is transferred in an average collision (18, 162). Winter (189) has found a similar temperature dependence in CO_2 and has suggested that energy transfer requires a finite time, so that efficient collisions should be fast, but not excessively so. Thus when chemical effects are present the Landau-Teller criterion of fast collisions, discussed previously, is no longer valid (15, 65). Such effects can be quite important in polyatomic molecules and are difficult to analyze theoretically.

A final point is that usually collisions with foreign gases are more effective in dissipating vibrational energy than self-collisions (15, 65). This is expected to be

true if (a) the foreign molecules are very light, so that they move faster at a given temperature and give faster collisions, (b) there is chemical affinity, or (c) there is close energy resonance between the two species (15).

5. Theory

Although conservation laws preclude exchange of energy between rotational modes or from rotation or translation to another degree of freedom in an isolated polyatomic molecule, it is not apparent that any such restrictions hold for transformations between vibrational modes or between electronic and vibrational degrees of freedom. Considering the former, it is claimed (143, 162) that rapid redistribution of vibrational energy among the vibrational modes—due to coupling between these modes and not collisions—occurs following excitation, presumably consistent with conservation of energy. During this postulated game of musical chairs the molecule may emit a photon, but this will very likely occur from a nuclear configuration quite different from that present during absorption. Consequently, the emission will not merely consist of reverse transitions to the lowest vibrational level of the ground state, but will also include transitions to the other ground vibrational states, as determined by Franck-Condon factors. This may explain the diffuseness of some polyatomic emission spectra.

A very important process arises when there is a *change in electronic state*. This can occur because the unique association of a vibronic level to an electronic state is blurred by vibronic coupling, especially among excited states. If the final state has the same multiplicity as the initial one, the process is called *internal conversion*.¹ If the multiplicity is different, it is called *intersystem crossing* (see Table I).

In a picture similar to one discussed earlier for collisions, the states of a polyatomic molecule are often said to be represented by potential surfaces in a multi-dimensional hyperspace, with the number of dimensions equal to the number of independent interatomic distances plus one for the energy (102). In this scheme, the actual configuration of the molecule is represented by a point which moves over the potential energy surface.² Internal conversion occurs when this point passes from one surface to another. For this to happen, the two surfaces should cross and a moderate interaction should exist between the two states at the inter-

section (149, 158). Absence of luminescence is often attributed, then, to a crossing of the excited state potential surface with that of the ground state. Because of the dense distribution of excited states, crossing of the surfaces for higher excited states is considered a frequent occurrence. More recent theories, to be discussed in section IV, allow transitions to occur even in the absence of curve crossings.

TABLE I

TYPES OF INTRAMOLECULAR RADIATIONLESS TRANSITIONS

Intrastate conversions (change in electronic state)	Intrastate conversions (no change in electronic state)
Internal conversion	Relaxation $\left\{ \begin{array}{l} \text{rotational} \\ \text{vibrational} \end{array} \right.$
Intersystem crossing	Vibrational rearrangement
Predissociation	Predissociation (63b)

Although we have regarded internal conversion as purely intramolecular, the environment (here, collisions) may act as a catalyst which increases the rate, or as a heat bath which removes excess vibrational energy and makes the process irreversible. As in the conversion of electronic energy to translational energy, the process of internal conversion is supposedly more difficult when more electronic energy is converted to nuclear vibration energy.

III. LIQUIDS

A. GENERAL COMMENTS

Almost all experimental work on radiationless transitions of molecular systems in liquid phase has been done on polyatomic molecules. In this subsection, the liquid and gaseous phases are compared. The next two subsections are devoted to two topics which have dominated research, the triplet state and energy transfer.

In comparing the liquid and gas phases it is convenient to consider that a certain collision rate prevails in a liquid, although the idea is less valid than it is in a gas. Thus it is known that a small molecule in a gas at STP experiences approximately 10^{10} collisions/sec.; a corresponding molecule in a liquid may be thought of as experiencing about 10^{13} "collisions" in this time (6). One result is that since many effective, perturbing collisions occur during the time necessary for a single rotation, rotations are generally suppressed in liquids. Vibrations are not so affected, both because of their characteristically shorter periods and the associated fact that vibrational energy is less readily transferred in collisions (6). Thus in absorption spectra vibrational but not rotational structure is observed. (The consequences of the presence in liquids of protean-ordered and -unordered regions (55) seem not to have been investigated.)

Emission spectra are seriously affected by this change in collision rate. Thus, though resonance radiation is

(1) There is considerable confusion in the use of the term *internal conversion*. Here, in the chemical physics definition, electronic energy is converted to vibrational energy. Kasha (81) uses the term to refer to processes with no spin change, while Sporer (158) applies it to processes that are not dissociative. Often the term is used not only for the isolated molecule energy-conserving process but also for fast vibrational relaxations that may follow. We have used a narrow definition of the term: isoenergetic, no multiplicity change, no dissociation.

(2) This should not be taken too literally since it involves a violation of the uncertainty principle. One may prefer to consider a fuzzy ball or an amoeba-like probability distribution, crawling over the potential surface.

observed from some gas phase polyatomic molecules, it is never observed in liquids. Instead, two rules have been formulated which summarize a vast number of observations: (1) The emitting level of a given multiplicity is the lowest excited level of that multiplicity (81). (2) The character of the emission spectrum of a substance does not depend on the exciting wave length.

These two rules form the observational basis for the belief that a molecule excited to a higher singlet state rapidly relaxes to its lowest excited singlet state, from which all further transitions proceed. Because these relaxation processes are so fast and because they do not provide radiation or any other suitable "handle" by which they may be studied, it has been difficult to make meaningful estimates of their rates. Surely they are much faster than the radiative rates of roughly 10^8 and 10^9 sec.⁻¹ with which they compete. Assuming that emissions from higher excited states as small as 10^{-4} of the normal fluorescence intensity would not have escaped detection, Kasha has estimated that the radiationless rates are at least 10^4 times as great as the radiative rates (81), *i.e.*, about the same as collision rates.

Because of the importance of these two rules, exceptions are of great interest. Out of hundreds of investigations, only two exceptions to rule 1 are known. Azulene is the most famous and best verified example (9, 158). This molecule is observed to fluoresce from its second excited singlet state and shows no emission from its lowest excited singlet. This anomalous behavior has now been observed in solution, in rigid glass at 77°K., in the gas phase, and in a mixed crystal. A number of possible explanations for this unusual emission have been presented (158). Several of these call attention to the relatively large energy separation between S_1 and S_2 and essentially rely on the precept that internal conversions involving a large change from electronic to vibrational energy are not favored. The absence of first singlet emission is interpreted as indicating an intersection of the potential surface of that state with that of the ground state. Recently, several more quantitative explanations have been given (69, 70, 150).

Scott and Becker (153b) have observed an emission, interpreted as phosphorescence, which occurs in ferrocene when that compound is illuminated in its second absorption band. No emission is observed when the lowest absorption bands is excited. Ferrocene is a so-called "sandwich compound" and consists of an iron atom located between two five-carbon rings (5). An emission had also been reported (146) from a naphthalene triplet later shown (106) not to be the lowest triplet, but this emission has now been attributed to a photochemically produced impurity (27b).

From rule 2 one can deduce that the *excitation spectrum*, which is obtained by monitoring emission as a function of exciting wave length, should be identical

with the absorption spectrum. This has been demonstrated for many compounds and implies that relaxation rates from higher states are much faster than competing intersystem crossing or predissociation rates. Deviations are often attributed to such phenomena as tautomerism, dimer formation, or the possession of more than one chromophoric group.

If intersystem crossing between higher states occurs, it should cause a variation in the ratio of the phosphorescence and the fluorescence quantum yields, Φ_p/Φ_f , with exciting wave length. Such a variation has been discovered for eosin in solutions at room temperature by Parker and Hatchard (126), and these authors mention similar findings in rigid medium by Bauer and Baczynski. Ferguson (48) has also reported studies of fluorescence and phosphorescence yields. He observed a decrease in Φ_f for 9,10-dibromoanthracene at shorter wave lengths and noted two different regions. These he interpreted as due to competition from predissociation of a C-Br bond and intersystem crossing. This effect was not observed in the analogous chlorine compound. Other variations were found in α -iodonaphthalene phosphorescence in rigid glass and in the fluorescence of some aromatic crystals upon cooling. This effect has also been demonstrated in chrysene and hexahelicene in rigid glass solutions at 77°K. (123), where Φ_p/Φ_f was found to increase when higher excited singlet states were excited. This may be due to efficient intersystem crossing between a higher singlet state and a close-lying triplet.

Bäckström and Sandros (4) have made some clever calculations which indicate that in biacetyl vapor radiationless transitions to the ground state occur from higher vibrational levels of the triplet. They suggest that this is the cause of the low phosphorescence yield of the gas relative to the liquid, where more rapid collisional deactivation of the higher states is expected. Their calculation assumes that the lifetime observed in EPA at 77°K. is the natural radiative lifetime.

In studies of nonresonant luminescence, measurements of lifetime give valuable information on radiationless transition rates. Quantum yields, which have been measured by Weber and Teale (179) in many systems, are also very useful.

B. THE TRIPLET STATE AND LONG-LIVED LUMINESCENCE

1. Phosphorescence

Interest in the triplet states of molecules has grown considerably since Lewis and Kasha (94) identified the phosphorescent "metastable state" proposed earlier by Jablonski (74) as a triplet state. The *lowest triplet state* of a molecule is of particular importance because of three distinguishing features (142): (1) it is usually the lowest excited state of the molecule; (2) it has a very

long lifetime in comparison with other excited states; (3) it is a distinct chemical species, often very reactive. Lewis and Kasha (94) discussed several features which distinguish this triplet emission from fluorescence; *e.g.*, the phosphorescence bands (as observed in a low temperature glass) are narrower and generally show different vibrational structure. They also noted that within a given class of molecules, the phosphorescence lifetime is shorter the longer the wave length of the emission (94, 106).

Phosphorescence is not to be expected from saturated molecules because of the disruptive effect which the production of two electrons with parallel spins would have upon the bonding structure in this type of molecule (94). Consequently, phosphorescence is more or less confined to molecules with double bonds, which can more easily accommodate the unpaired electrons. Also, this emission process is greatly enhanced when the lowest *singlet* state is of the (n, π^*) type. El-Sayed has suggested that this effect is due to intersystem crossing to the (π, π^*) (and not (n, π^*)) triplet, and that, in general, there is "no spin orbit coupling between singlet and triplet states of the same configuration" (45). He has applied this analysis to explain the phosphorescence properties of the diazines (43). It also explains an interesting solvent effect in quinoline, where the lowest singlet (π, π^*) and (n, π^*) states are close in energy. For this compound in the vapor phase (47) and hydrocarbon glasses (43) the (n, π^*) state is lowest and only phosphorescence is observed; in hydroxylic glasses, where the (π, π^*) singlet is lowest, both fluorescence and phosphorescence are observed (47). A similar explanation has been given for the fluorescent properties of chlorophyll (8), but recent studies imply that solvent effects on aggregation may play a dominant role for that compound (29).

For most molecules phosphorescence may be observed only in a rigid glass environment at low temperature, but some substances also phosphoresce in the gas and liquid phases. Perhaps the best known of such substances is biacetyl, which phosphoresces in all three phases. Other examples of liquid phase phosphorescence include eosin (in glycerol and ethanol) (95, 126) and certain dyes (in H_2O and propyl alcohol) (95). One reason that so few substances phosphoresce in solution is that the long lifetime of the triplet makes it highly susceptible to quenching before it radiates. In solid solutions this diffusional quenching is eliminated. The most notorious culprit by far in the quenching of triplet species is molecular oxygen. Nitric oxide, another paramagnetic gas molecule, displays quenching abilities similar to those of oxygen (140).

2. Experimental Methods: Triplet-Triplet Absorption

Spectroscopic studies of triplet states are of four principal types: (1) singlet-triplet absorption, (2)

triplet-singlet emission, (3) e.s.r. measurements, and (4) triplet-triplet absorption. Direct absorption experiments are difficult because singlet-triplet absorptions are highly forbidden by as large a factor as 10^8 and hence are easily obscured. Emission studies are generally limited to rigid glasses. E.s.r. measurements on triplet states were pioneered by Hutchison and Mangum (71), who first measured the paramagnetic resonance of naphthalene as a substitutional solid. The method has been gradually extended to less restrictive circumstances than a substitutional solid. So far the most general technique has been the study of triplet-triplet absorption spectra.

Triplet-triplet absorption studies are made by studying the change in the absorption spectrum after a strong flash of light. A very high fraction of the solute can be excited to the triplet state. Such studies not only determine the absorption spectrum of the triplet state, but also determine its concentration as a function of time. The method is said to be equally useful for gases, liquids, and solids (137). Although the flash sometimes causes photodecomposition (85), in other cases repeated flashes remove troublesome traces of oxygen (139).

Triplet-triplet absorption spectra were first taken by Lewis. Porter and Windsor (139) have monitored the change in spectrum with a second flash that follows the first after times of 30 to 300 $\mu\text{sec.}$ and is detected photographically. Linschitz and his co-workers (96-98, 133, 159) have monitored with a beam of light sent through a monochrometer and detected photoelectrically. These spectra have now been obtained for a variety of compounds (94, 137, 139, 140).

One very interesting and still unexplained anomaly disclosed by these experiments is the absence of triplet-triplet absorption bands for benzene, although these have been searched for in the gas, liquid, and rigid solvents (85, 140, 141). Certainly the triplet is populated in the rigid solvent, where strong phosphorescence is observed, and calculations by Pariser (129) indicate a triplet level within the range studied.

3. Delayed Fluorescence

The presence in some compounds of long-lived luminescence, called "delayed fluorescence," at the same wave lengths as normal fluorescence has been known for some time. At least three distinct mechanisms have been suggested for this process under different circumstances: dimer formation (50, 186), thermal re-excitation from the triplet (94, 126), and triplet-triplet interaction (2, 86, 127, 128, 148, 167, 170). Delayed fluorescence has now been observed in vapors (166, 186), liquids (50, 126-128, 167), rigid glasses (2), and molecular crystals (86). Lewis and Kasha (94) noted in 1944 the distinction between normal phosphorescence and " α -afterglow," a long-lived tempera-

ture-dependent emission occurring at fluorescence wavelengths. This afterglow results from thermal excitation of molecules from the triplet to the lowest excited singlet and has been named "E-type" delayed fluorescence by Parker and Hatchard (128) because of its occurrence in eosin. It is only possible when the triplet level is close in energy to the singlet.

In 1962 Parker and Hatchard (126), in studies of anthracene and phenanthrene in solution, observed that the intensities of both delayed and sensitized fluorescence varied as the square of the incident light intensity. This led them to suggest that a bimolecular interaction between two triplet molecules was occurring, resulting in the formation of an excited singlet molecule and a normal molecule. Anthracene is an especially favorable case for this since the singlet energy is approximately twice that of the triplet. If this is the case, the time constant for the delayed fluorescence, τ_D , should be equal to one-half the triplet-state lifetime, τ_T (128). Stevens and Walker (167) have very recently shown this to be true. Because of its occurrence in pyrene this type of luminescence has been designated "P-type" delayed fluorescence (128).

Parker and Hatchard's suggestion involves the intermediate formation of dimers, perhaps very short-lived, and they suggest that this mechanism may also account for some vapor phase results previously attributed to dimer formation between an excited molecule and a ground-state molecule. It should be noted that dependence on the square of incident light intensity or even on the square of phosphorescence intensity (which may well just reflect the former dependence) would also apply to other two photon processes such as the absorption of two photons through real or virtual states of the molecules (150). Studies of the time dependence of the emission can often eliminate this ambiguity (86).

Robinson and his co-workers (148, 150, 161) have discussed triplet-triplet interaction (annihilation) processes in great detail. Their approach indicates that relatively long-range interactions can occur through virtual states of the host molecules.

4. Intersystem Crossing

a. Anomalous Viscosity Dependence

The phenomenon of intersystem crossing has provided many puzzles for molecular spectroscopists. Consider the energy levels for a molecule as represented in Figure 3. One of the most puzzling observations has been the apparent viscosity dependence of the radiationless transition from the lowest triplet to the ground state ($T_1 \rightarrow S_0$) (68, 98, 142). It is difficult to understand why this process should depend on viscosity, while the rate of $S_1 \rightarrow T_1$ does not. Recent work has explained this phenomenon (68, 76, 77, 97, 98, 140-142, 159).

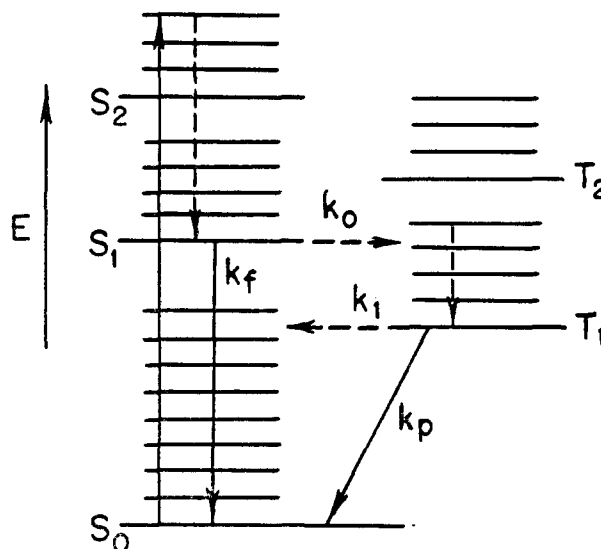


Figure 3.—Schematic representation of molecular energy levels and transitions.

The decay of triplet states in solution may be conveniently described by the equation (68)

$$-\frac{d[T]}{dt} = k_p[T] + k_1[T] + k_2[T]^2 + k_3[T][G] + \sum_q k_q[T][Q]$$

where T and G represent the triplet and ground states, respectively, and k_p , k_1 , k_2 , k_3 , and k_q are rate constants for phosphorescence, intersystem crossing $T_1 \rightarrow S_0$, triplet-triplet quenching, self-quenching by a ground-state molecule, and the action of other quenchers, Q, respectively. Often contributions from the third and fourth terms on the right can be made small (*e.g.*, by using low concentrations). In this case contributions to the observed first-order decay arise from k_p , k_1 , and k_q . It is now felt (68, 76, 77, 98) that the observed viscosity dependence is due to contributions from such pseudo-first-order terms as k_q , which arise from inevitable traces of foreign substances, *e.g.*, oxygen.

This conclusion has made it possible to obtain some (approximate) true first-order rate constants. Studies in eosin (126) have shown that $T_1 \rightarrow S_0$ is independent of viscosity as long as the solution is not rigid. The rate, in glycerol or ethanol at 20°, was found to be about $2.5 \times 10^2 \text{ sec}^{-1}$, while $k_0(S_1 \rightarrow T_1)$ was roughly 10^7 sec^{-1} .

In earlier studies, Porter and Wright (141, 142) found that for aromatic hydrocarbons k_0 averaged about 10^8 sec^{-1} , while k_1 was often less than 10^{-1} sec^{-1} in rigid media. The condition that the $T_1 \rightarrow S_0$ radiationless transition is greatly retarded in rigid media allows phosphorescence to be seen there. Of course, a good deal of the effect of a rigid medium is due to the trapping of the quenchers. However, the low temperatures used also inhibit energy transfer (94, 104). When this occurs some molecules which have crossed over to the

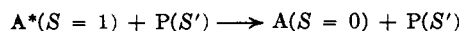
singlet from the triplet may return again to the triplet and thereby increase the phosphorescent yield. This effect has been inferred at 20 and 4°K. by Kasha and McGlynn (85).

It is usually possible to measure the *intrinsic* radiationless rate, k_1 , only when it is the dominant process. Hoffman and Porter (68) have studied halogenated polyacenes, where the heavy-atom-induced spin-orbit coupling can be expected to cause high intersystem crossing rates. In only one case, 9,10-dibromoanthracene, were they able to exceed the external quenching rates. For this compound a change in solvent viscosity by a factor of 170 left the first-order rate unchanged. They also reported observations on the effectiveness of halogen substitution in anthracene derivatives. It was found that bromination causes rates ten times faster than does chlorination, and halogenation at the 9,10-positions is four times as effective as at other positions.

Hoffman and Porter feel that many published results are incorrect because several features have not been recognized (68). One of these is the great effect of O₂ on the integrated absorption for S → T transitions—this has led to spuriously high values for $k_p = 1/\tau_p$. Secondly, phosphorescence decay times in rigid media are sometimes assumed to be determined by natural radiative decay process, whereas, in fact, k_1 may often exceed k_p in these situations. Finally, it should be recognized that at present it is not possible to remove all quenching impurities completely, and the effect of these is often important.

b. Quenching by Paramagnetic Substances

Although oxygen is the best known quencher of the triplet state, it is found that all paramagnetic substances are effective in this function (96, 97, 137, 159). Furthermore, studies of quenching by transition metal ions (96, 97, 159) have demonstrated that quenching ability is not directly related to the number of unpaired spins or magnetic susceptibility of the quenchers, and therefore quenching cannot be simply attributed to an effect of the magnetic field of the ion (97, 137). Porter and Wright have proposed (142) that the function of the paramagnetic quencher is to allow total spin conservation in the collisional deactivation process. Thus the process



is spin-allowed if the spin quantum number, S' , of P is greater than zero. Hence differences in quenching efficiency may be attributed to differences in exchange interaction in the collision complex, which is determined by electronic orbital overlap between the collision partners (142). Linshitz and Pekkarinen (97) have pointed out other factors, such as solvation, which affect this process.

c. Differences in Intersystem Crossing Rates

It is still not clear why the process S₁ → T₁ should be 10⁴ to 10⁶ or more times as fast as the T₁ → S₀ transition. The simplest explanation, that S₁ and T₁ are usually closer in energy than T₁ and S₀—so that more “Teller crossings” of S₁ and T₁ are expected and less energy need be changed from electronic to vibrational form—has provided a qualitative theme for a number of later ideas.

One such explanation is that the initial intersystem crossing occurs between S₁ and some higher triplet T₂ whose energy is close to S₁. Such triplets are often predicted in molecular-orbital theory, although they are difficult to determine experimentally. Radiationless transition to such higher triplets requires very little conversion of electronic to vibrational energy. Pariser (129) has suggested that in addition the “plus” or “minus” character of alternant hydrocarbon electronic states, which plays a role in optical transition selection rules, may be important for intersystem crossing.

Robinson and Frosch (150) have explained this difference as due in large extent to vibrational overlap factors, which are expected to become smaller with larger energy gaps between electronic zero-point energies. (Their theory is discussed further in section IV.) A striking example of the presumed effects of overlap factors has been given by Wright and these authors in the effect of deuterium substitution on the phosphorescence lifetimes of benzene in several rare gas “solvents” at 4.2°K. (190). Observed radiative decay times for the deuterated compound were found to be two to three times as long as for normal benzene. Apparently this is due to the smaller overlap factors in C₆D₆, which retard the radiationless triplet decay and thereby allow the natural rate of the phosphorescence to be observed.

Franck and Sponer have proposed that a resonance mechanism similar to one proposed by Förster for *intermolecular* transfer (see section III,C,5) may be efficient as an *intramolecular* phenomenon (54). This “internal sensitization” could readily occur between the second and first excited singlet states, for example, and also between the first excited singlet and the triplet state. However, one would not expect such an interaction with the ground state, the authors assert, because the ground state lacks the requisite properties of a “variable electronic resonator” whose frequency range overlaps that of the other state. They indicate that the interpretation of radiationless transitions as due to internal sensitization is consistent with the view of intersection of potential surfaces.

5. Other Triplet-State Phenomena

While intramolecular spin-orbit interactions are generally dominant in determining intrinsic intersystem crossing rates, *intermolecular* spin-orbit effects can modify these *intrinsic* (as opposed to external

quenching) rates in special circumstances (84, 190). Kasha has given a striking example of this in the effect of ethyl iodide upon naphthalene derivatives (82). He found that when solutions of ethyl iodide and α -chloronaphthalene, both colorless, are mixed the resulting solution is yellow, and that this change results from the enhancement of a formerly very weak singlet-triplet absorption. This he interprets in terms of a so-called "static" component in the collisional spin-orbit perturbations, a term which arises from the cage effect in liquids. It is pointed out that the effectiveness of alkyl halides in quenching the fluorescence of aromatic hydrocarbons in solution is known to be in order $I \gg Br > Cl > F$, and this may be attributed to the same cause. Also an intermolecular heavy-atom effect has been observed on the phosphorescence lifetime of benzene in several rare gas solids at very low temperatures (190).

Some compounds are observed to show changes in coloration upon heating or illumination (22). These phenomena, called thermochromism and photochromism, can also be associated with intersystem crossing in some cases. Grubb and Kistiakowsky (60) have shown that the thermochromism of bianthrone is due to thermal population of the lowest triplet from the ground state, which allows triplet-triplet absorptions to occur. This conjecture is supported by e.s.r. studies (121). It has been suggested (106) that such an effect might occur also in the higher polyacenes.

McRae and Kasha (107) have predicted that the phosphorescence yield of dye molecules may often increase upon aggregation. They suggest that the spreading of singlet levels into bands should increase $S_1 \rightarrow T_1$ intersystem crossing, while splitting in the triplet is expected to be relatively slight. The consequences of the geometrical arrangement of the monomers in the aggregate have also been discussed by these authors.

C. ENERGY TRANSFER

1. Intramolecular Energy Transfer

Numerous examples of energy transfer between different parts of complex molecules have been observed. Transfer between aromatic amino acids in proteins is an example of this and has been discussed by Stryer (169). In this case a resonance-transfer mechanism is favored.

Another familiar example is the photoinduced dissociation of carbon monoxide from myoglobin (23) and other heme proteins (see references in (52)). This occurs with equally high efficiency regardless of whether the light is absorbed in the heme or in the protein component. Energy transfer has also been studied between chelating molecules and their coordinated metal ions (33, 46), where it often leads to line emission from the ions.

Another type of system in which intramolecular transfer has been studied uses double molecules formed by joining two molecules (usually aromatics) by a saturated link with one to several carbon atoms (30, 152). Schnepf and Levy (152) have found that joined naphthalene and anthracene show transfer efficiencies at least ten times as great as in a comparable solution. No information on the distance dependence of transfer was obtained here because of the flexibility of the connecting links.

2. Sensitized Fluorescence and Related Phenomena

The study of fluorescence in solution has yielded information about energy transfer between identical molecules. It is found that with increasing concentration there is (1) a decrease in the quantum yield of fluorescence and (2) a concurrent loss of polarization in the fluorescence (175).

Both of the effects can be attributed to energy transfer. The first effect is called *self-quenching*. A possible explanation of the role of excitation transfer here is that increased transfer enlarges the probability that the excitation will visit a quenching site. This site may be a nonfluorescent dimer, a dye molecule with a nearby impurity, or some other entity.

The depolarization may be explained by increased excitation transfer, since the orientation of the oscillator of the emitting dye molecule will very likely differ from that of the absorbing molecule. In reasonably viscous solutions Brownian rotations of the dye molecules are not important during the lifetime of excitation. An interesting corollary to this effect is the observed depolarization of fluorescence during the *time* course of emission, as observed by Vavilov (178) and others (75, 91).

Birks and his co-workers (12, 14) have studied the effects of dimer formation on the fluorescence properties of aromatic hydrocarbons in solution. In particular they have described the emission properties of "excimers," which are dimers formed by an excited and an unexcited molecule and which dissociate upon emission (13, 165). They have also discussed various concentration-dependent effects on both absorption and emission properties in terms of the formation of different types of dimers (13).

Sensitized fluorescence is often used to study transfer of excitation between singlet states of different molecules. Biacetyl fluorescence may be sensitized by a number of other substances (39, 40). The results indicate that a diffusion-controlled transfer, and not a longer range resonance transfer, is involved. A collision mechanism has also been implicated in other systems (17).

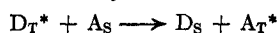
In some instances of sensitized fluorescence it is possible to follow the increase in τ_A (acceptor lifetime) and decrease in τ_D (donor lifetime) as the concentration of

acceptor is increased (57, 151). It is often found that the decline in τ_D is not as rapid as the concentration quenching of the fluorescence (172). This should not be unexpected if reabsorption is occurring, which would seem likely for the concentrated solutions used.

In this regard, Weinreb (180) has proposed a method for distinguishing between radiationless and radiative (by reabsorption) energy transfer. He suggests using a strong quencher of the donor fluorescence and analyzing the resultant effect on the excitation-transfer process to determine the relative contribution of the radiative process. Fluorescence quenching by itself is often used to indicate energy transfer when the acceptor is not fluorescent.

3. Triplet-State Energy Transfer

The first clear demonstration of transfer of energy between triplet states of molecules was made in 1952 by Terenin and Ermolaev (173) with observations of sensitized phosphorescence in rigid media. The process may be represented by



In these systems the energy transfer occurs at short distances and has been attributed to exchange terms which depend on the overlap of electron clouds. Calculations by Förster indicate that for these forbidden transitions the dipole-dipole terms are small (52) and other interactions, such as exchange, should then be considered.

Subsequent studies have demonstrated sensitized phosphorescence in many systems. Work prior to 1956 has been summarized by Terenin and Ermolaev (175). In some cases quantum yields *via* a sensitizing molecule are even larger than those obtained by direct absorption of light by the acceptor molecule. The shortening of donor lifetimes due to the transfer process has also been observed (174, 175; but see 156). One criterion for energy transfer is that the donor energy state should be higher than that of the acceptor (175). Terenin and Ermolaev used compounds with energy states as represented in Figure 4, so that energy transfer through the acceptor singlet was not possible (174, 175). El-Sayed and Bhaumik have used such a system to sensitize emission from a chelated ion by triplet transfer from benzophenone to the chelate (46).

Because biacetyl phosphoresces strongly in solution it is often used in triplet energy-transfer experiments in liquids. It has been used as an energy donor in observations of quenching of phosphorescence (3) and as an acceptor in sensitized phosphorescence experiments (4). In the former study, two distinct classes of quenchers were noted: the first class of molecules contains loosely bound H atoms, which apparently are abstracted by biacetyl upon collision; in the second class are unsaturated hydrocarbons, which act by the triplet-triplet mechanism described previously. In

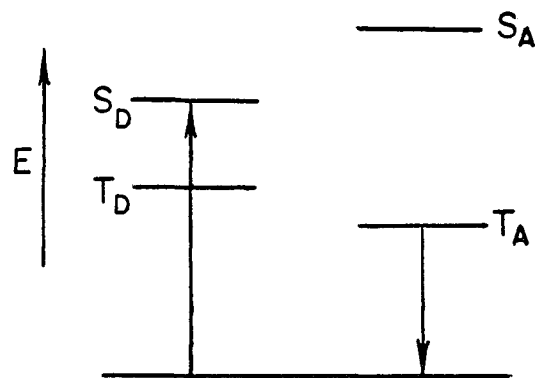


Figure 4.—Energy levels for energy transfer *via* triplet states.

the latter investigations, benzophenone was used to sensitize phosphorescence in biacetyl and other compounds (4).

Berends and Posthuma (10) have utilized paramagnetic quenching effects to implicate a triplet-triplet transfer mechanism in the photosensitized decomposition of a polyene fungicide. It is known that illumination with visible light of an aqueous solution of the antibiotic pimaricin causes destruction of the pimaricin if either riboflavin or lumichrome is present. Since pimaricin does not absorb in the visible region, energy transfer from a sensitizing molecule is indicated. Because of the short lifetime of the sensitizer singlets, it seemed unlikely that these states could be involved. The suspicion of triplet-state involvement was greatly strengthened by the suppressing effect of paramagnetic quenchers on the photodecomposition, which was seen to parallel their effect on sensitizer phosphorescence.

Also, it may be recalled that the gas phase work of Noyes and others (72, 130, 132) indicated that benzene triplets were responsible for the sensitized phosphorescence of biacetyl. Quite recently, studies of the corresponding process in solution have been made in order to establish the existence of benzene triplet molecules in liquids. In keeping with precedent, unusual results have been obtained. Lipsky (100) has reported that in degassed cyclohexane benzene-sensitized biacetyl phosphorescence occurs, indicating that triplet benzene is present. At the same time, Dubois and Wilkinson have been unable to detect any such process in aerated or deaerated hexane solution (41). At 77°K., however, they report that triplet-triplet transfer occurs, apparently by a resonance mechanism, with $R_0 = 11 \text{ \AA}$. (see section III,C,5).

4. Heterogeneous Systems

Investigations of energy transfer in heterogeneous systems, in which one component is dissolved and another suspended in solution, have been made by Moodie and Reid (112). Effects observed in these systems have been attributed by the authors to adsorption of molecules of one type onto microcrystals of the

other component. Terenin and Ermolaev (175) have disagreed with this interpretation and have discussed these results in some detail.

5. Mechanisms of Energy Transfer

In distinction to cases in which the environment acts as a passive receiver of energy (usually in small packets), two molecules may interact sufficiently so that considerable energy is transferred from one to the other. Often, but not always, this occurs from thermally relaxed vibrational levels of the lowest singlet or triplet state of the molecule, the entire electronic energy being transferred in the process. Four main mechanisms have been proposed for such energy transfer between solute molecules in the liquid state. Their relative importance varies widely with the particular system under investigation.

a. Collisions

This is obviously a short-range interaction. With unit transfer efficiency on collision, the rate of this transfer is given by the Debye equation (39) as

$$K = \frac{8RT}{3000\eta} \text{ (l. mole}^{-1} \text{ sec.}^{-1}\text{)}$$

where R is the gas constant (in erg/deg.-mole) and η is the viscosity in poise. Modifications of this formula for the cases of collisions of unequal-sized spheres and the inclusion of an interaction potential have also been given by Debye (36). (For situations where this applies see ref. 39, 138, 139.)

b. Emission and Reabsorption of a Photon

This is a long-range interaction and depends on the overlap of donor fluorescence and acceptor absorption. Often this is not very efficient; an upper limit to the efficiency is determined by the fluorescence yield of the donor and the absorption coefficient of the acceptor. This mechanism is invariably referred to as the "trivial process," presumably in reference to the ease of explanation rather than lack of importance (101, 180).

c. Dimer Formation

This is a variation of mechanism a and may be considered as a long-lived collision complex (128).

d. Resonance Transfer (Förster Transfer, Inductive Resonance)

Transfer may occur over moderate distances, 10–60 Å, being common. This mechanism was originally proposed by J. Perrin in terms of the classical inductive coupling of two identical oscillators. It was later modified by F. Perrin, but both theories predicted distances larger than those observed (175). Förster (49a, 51, 52) has given a quantum mechanical treatment of this phenomenon, which takes into account the

lack of exact energy resonance between absorption and emission oscillators. The interaction is of a dipole-dipole variety similar to that in dispersion forces. Most simply, the transfer rate is given by

$$R = \frac{1}{\tau} \left(\frac{R_0}{R} \right)^6$$

where τ is the actual mean life of the donor (sensitizer) and R_0 is the "critical transfer distance" at which resonance transfer is 50% probable. The efficiency of transfer, as characterized by R_0 , depends on the relative orientation of the two oscillators and on the overlap of the donor fluorescence and the acceptor absorption spectra. The expression is (52)

$$R_0^6 = \frac{9000(\ln 10)K^2\eta_D^\circ}{128\pi^6n^4N} \int_0^\infty f_D(\nu)\epsilon_A(\nu) \frac{d\nu}{\nu^4}$$

Here η_D° = the donor fluorescence quantum yield (in the absence of transfer), n = the refractive index, N = Avogadro's number, the integral is the overlap of donor emission and acceptor absorption, and K^2 depends on the orientation of the two dipoles ($K^2 = 2/3$ for a random distribution). Transfer is efficient only for allowed transitions.

The existence of other mechanisms is sometimes suggested. Dexter has considered a number of these in a somewhat different context (37). Whether excitons can exist in liquids remains largely unstudied (67). Since exciton transfer depends very critically on exact degeneracy of subunits, no such transfer is expected except between identical molecules (67). From the theoretical standpoint excitons arise as first-order perturbation terms and depend on integrals of the form $(\psi|M|\psi')$, where M is the dipole interaction operator. The result is a distance dependence of the form $1/R^3$ for transfer. This is in contrast to the Förster mechanism, which arises from second-order perturbation terms of the form $(\psi|M|\psi')^2$ and predicts that transfer probability should depend on the inverse sixth power of the distance.

IV. DISCUSSION OF THEORIES

In this paper two major variations have been discussed: an increasing complexity of the solute molecule and an increasing collision rate as the environment changes from a low pressure gas to a liquid. Atoms and the simpler molecules show sharp resonance emissions, while in complex molecules emission can be diffuse, nonresonant, or lacking even at low pressures. As pressure increases there is a trend toward relaxation of the different degrees of freedom, until in the liquid emissions are observed from the lowest excited states almost without exception. Since most experimenters have worked either with small molecules at low pressures or with complex molecules in liquids, in practice the distinct contribution of molecular complexity to

radiationless transitions has not been clearly separated from that of increased collision rate. Some approaches to this problem will now be given.

One approach that has proved very fruitful is that of Kasha and his students. They have emphasized the importance for luminescence properties of the interrelations among the lowest excited states: the relation of singlets to triplets, (π, π^*) to (n, π^*) states, etc. Empirical rules have been formulated and given qualitative rationales. Underlying this scheme is the well-supported assumption that relaxation to the lowest vibrational level of a given electronic state is very fast.

This approach might be formalized somewhat by assuming that in the absence of restrictions a basic transition rate, on the order of 10^{14} sec.⁻¹, is present (69). This rate is reduced by certain types of restrictions such as:

(1) Spin change. This has been estimated by Kasha (80) to impose a restriction of 10^{-6} on intersystem crossings relative to internal conversions.

(2) Franck-Condon vibration overlaps. These depend on a host of factors such as the electronic energy difference between the two states, the shape and relative displacement of the potential curves for the states, and effects of the environment. Values have been estimated to run from almost unity down to 10^{-10} and lower for different problems (150).

(3) Same configuration restriction. El-Sayed (45) has calculated that intersystem crossings between singlet and triplet states of the same configuration are forbidden in first order and has suggested, *e.g.*, that crossing between two (n, π^*) states might be roughly 10^3 times slower than the comparable $(n, \pi^*) \rightarrow (\pi, \pi^*)$ transition.

(4) Other restrictions (?). Symmetry, temperature effect, etc., are sometimes mentioned.

More quantitative approaches to radiationless transitions in condensed media have been formulated recently. These approaches take different views of the relative importance of conditions internal to the molecule, on the one hand, and of environmental interactions, on the other.

Hunt, McCoy, and Ross (69) have developed a theory that ignores environmental effects except that vibrational relaxation is assumed to be fast. Their theory treats internal conversions in aromatic hydrocarbons in terms of a single parameter—the root-mean-square change in bond length upon excitation. This had previously been employed to explain the vibrational structure of certain radiative transitions (105). From this they derive a “barrier” distance between the two states involved in the radiationless transition which is “the shortest (multidimensional) distance between the zero-point zone of the upper state and the isoenergetic section through the potential energy surface of the lower.” They use Pariser’s wave functions

and bond orders and apply Coulson’s empirical relation to obtain bond lengths. Using paraboloids of revolution for the potential energy surfaces, they obtain an empirical relation in which the tunneling rate shows a negative exponential dependence on the barrier width. A barrier width of zero corresponds to a Teller crossing at the lowest vibrational level of the primary state, and this is found to be a frequent, but not universal, occurrence. A prohibitive factor of 10^{-6} was used for transitions with a spin change. The authors feel that this method successfully explains the processes occurring in benzene, naphthalene, and anthracene.

Robinson and Frosch (147, 150) have proposed a theory in which the environment is more explicitly considered. They consider a system consisting of a solute molecule plus the surrounding solvent. Their zero-order states are nonstationary states of this system, and these develop in time as determined by relatively small time-independent terms (*e.g.*, spin-orbit coupling) in the full Hamiltonian which are initially neglected. The role of the solvent, through coupling to the solute molecule, is to provide a large number of possible final states nearly degenerate with the initial state. They feel that the rate-limiting step is internal, determined by factors already existing in the free molecule. They also feel that this theory explains the high rates of some intersystem crossing processes and the characteristically slower rates of the formally similar lowest triplet- to ground-state radiationless transition (150). Robinson and Frosch have extended their theory in detail to considerations of energy-transfer mechanisms. They stress the role of Franck-Condon factors and have given an approximate method for estimating these for some molecules in terms of the electronic energy gap between the states involved. In most situations treated by their theory they predict that temperature effects should be small.

An extreme environmental theory was put forth by Gouterman (59), who started with the assumption that in the absence of environment or of dissociative phenomena, there are no radiationless transitions. All radiationless transitions were presumed to proceed by the exchange of phonon energy with the environment in analogy to radiative processes in which photons are absorbed or emitted from the radiation field. Although only a crystalline environment was considered, the idea can be extended to other media by using a general theory of dissipation in quantum mechanics given by Senitzky (154). This theory treats the environment in general terms as a “loss mechanism,” which is not specifically defined other than to say that it has a large number of closely spaced energy levels and is relatively unaffected by the system subject to radiationless decay. Recent experiments on naphthalene fail to show temperature dependence such as Gouterman’s theory predicts (61).

To understand radiationless transitions in semi-isolated polyatomic molecules in condensed phases much further work is needed. Experimentally, studies of larger polyatomics in very low pressure gas phase and of small molecules in condensed phase would be useful, but these systems are difficult to prepare. In experiments of the first sort the environment is removed, while in the latter case the molecular system is greatly simplified. The recent discussion on the theory of radiationless transitions does seem to have stimulated renewed gas phase polyatomic low pressure work (131, 187).

Many theoretical questions also remain to be answered. We should like to know, for instance, whether the commonly observed absence of emission from excited states other than the lowest of each multiplicity can be completely explained in terms of the electronic energy gaps involved. Specifically, this asks whether the only reason that excited states are not observed to emit is that they are closer together, thus increasing the possibility of radiationless processes. Also, the mechanisms involved in many important energy-transfer situations remain to be defined. One helpful step here would be to obtain unambiguous determinations of distance dependences for specific systems. Solute-solvent interactions need a closer look. (Even Gouterman, whose theory is environmental, treated these interactions parametrically.) Also, more detailed knowledge on vibronic wave functions in polyatomic molecules will be required. And, of course, many peculiarities of individual compounds, such as the absence of triplet-triplet absorptions in benzene, remain more or less mysterious. These problems should keep the field interesting for some time to come.

V. REVIEWS AND GENERAL ARTICLES

Surveys and general discussions of problems related to energy transfer and radiationless transitions have been given in recent years by Franck and Livingston (53), Kasha (81, 83), Terenin and Ermolaev (172, 175), Dexter (37), Livingston (101), Spomer (158), Porter and Wright (142), Robinson (147, 149), and Förster (52). Often, if not defined explicitly, the assumption of a liquid environment is implicit. Lipsett has compiled an extensive bibliography of articles related to "Energy Transfer in Polyacene Solid Solutions" (99).

One strong motivation for the study of energy transfer in many of the above systems has been the possible extension of such investigations to systems of biological interest. For instance, sensitized fluorescence between accessory pigments and chlorophyll has been studied both *in vitro* and *in vivo* (42, 56). Energy transfer in biological systems cannot be discussed here, and only convenient starting points in the literature shall be noted. Volumes of the *Discussions of the Faraday Society* (No. 27, 1959) and *Radiation Research*

(Suppl. 2, 1960) have been devoted to this topic. Also the review of Terenin and Ermolaev (172, 175) contains helpful discussions of biological systems. Articles by Rabinowitch on "Photosynthesis and Energy Transfer" (144) and Stryer on "Energy Transfer in Proteins and Polypeptides" (169) might be of particular interest.

VI. THE LIFETIMES OF EXCITED STATES

If a process involving an excited state is to occur, it must be rapid enough to take place during the lifetime of the existence of the state. Conversely, the lifetime of an excited state is *determined* by the rates of those processes which depopulate it, and, if the lifetime is ascertained, it can give information about the rates of these processes.

Confusion may result from the fact that the term "lifetime" can refer to any of several times associated with the decay of an excited state. It may be helpful to identify these lifetimes with the experimental methods used to obtain them.

There are four main ways to measure lifetimes. (More esoteric methods are given in ref. 111.)

A. FROM THE INTEGRATED ABSORPTION

$$\frac{1}{\tau_0} = \frac{\bar{\nu}^2}{3.47 \times 10^8} \frac{g_l}{g_u} \int \epsilon \, d\bar{\nu}$$

(see 83 and references cited) or equivalently

$$f = \text{oscillator strength} = 1.500 \frac{g_u}{g_l} \frac{1}{\bar{\nu}^2 \tau_0}$$

where $\bar{\nu}$ is the wave number, ϵ is the molar extinction coefficient, and g_l and g_u are the degeneracies (or multiplicities) in the lower and upper states of the transition, respectively. Here τ_0 is the natural, *radiative* mean lifetime of an excited state free from intermolecular quenching. Only in rare cases does the environment influence this value (82, 88). In the strictest sense, this formula is valid only for distinct, narrow spectral lines, but it has sometimes been applied to molecular situations (95). Recently Strickler and Berg (168) have derived a better relationship, which may be used for the broad molecular bands of strongly allowed transitions. Their formula is

$$\frac{1}{\tau} = 2.880 \times 10^{-9} n^2 \langle \bar{\nu}_l^{-3} \rangle^{-1}_{av} (g_l/g_u) \int \epsilon \, d \ln \bar{\nu}$$

where n is the refractive index.

B. FROM THE UNCERTAINTY PRINCIPLE

$$\Delta E \Delta \tau \geq \hbar/2$$

$$\Delta \tau = \tau_1 \geq \frac{\hbar}{2 \Delta E} = \frac{1}{4 \pi \Delta \bar{\nu} C}$$

where ΔE = the r.m.s. energy width of the absorption. Here τ_1 is the r.m.s. value for the actual lifetime of the

state. This gives a lower limit to the actual lifetime. (In principle the line width is determined by the lifetimes of both states between which a transition occurs, but when one of these times is very long, as for the ground state, its contribution becomes negligible (1).)

Table II gives values for τ_1 and $\Delta\nu$ for illustration. It assumes equality in the above expression.

TABLE II
ENERGY LINE WIDTHS AND CORRESPONDING
TIME UNCERTAINTIES

τ_1 , sec.	$\Delta\nu$, cm. ⁻¹
10 ⁻¹⁶	26,500
10 ⁻¹⁴	265
10 ⁻¹²	2.65
10 ⁻¹⁰	0.0265

C. FROM THE OBSERVED DECAY SCHEME

If only first-order processes are important

$$-\frac{d[A]}{dt} = k[A]$$

and

$$[A] = A_0 e^{-t/\tau_1}$$

where τ_1 = the time it takes for the concentration of A to fall to 1/e of its original value. This is a measure of the actual lifetime and should fall between τ_0 and τ_1 above.

This may be measured by a number of techniques. Slow changes, $\tau > 10^{-3}$ sec., can be studied using mechanical choppers. For shorter times, 10^{-3} sec. $> \tau > 10^{-6}$ sec., flash techniques are used. For still shorter times Kerr cells and phase shift methods are employed. Either emission or changes in absorption may be monitored. The long-lived states are usually triplets.

D. FROM A STERN-VOLMER QUENCHING PLOT

Here the fluorescence yield is followed as a function of the partial pressure of an added quenching gas

$$\frac{I_0}{I} = 1 + \tau_0 Z_Q = 1 + \frac{\tau_0}{\tau_3 P} \quad (109, 111)$$

where P is the pressure of foreign gas in atmospheres, Z_Q is the number of effective quenching collisions per second, τ_0 is as above, and τ_3 is the time constant for the quenching reaction at $P = 1$ atm. This formula assumes that the only quenching process active is that caused by the foreign gas. Also Z_Q must be known if τ_0 is to be calculated (the kinetic theory formula for unit collision efficiency is sometimes used), or if τ_3 is desired, τ_0 must be known.

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