

THE PHOTOLUMINESCENCE AND ASSOCIATED PROCESSES OF COMPLEX ORGANIC MOLECULES IN THE VAPOR PHASE.¹

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CONTENTS

I. Introduction.....	439
II. The general photokinetic scheme.....	442
A. Excitation.....	443
B. First-order deactivation of the absorption product.....	445
C. Second-order deactivation of the absorption product.....	450
D. Fluorescence emission.....	451
E. Second-order deactivation of the fluorescent level.....	452
F. The overall fluorescence yield.....	453
III. The dependence of intensity of fluorescence on factors other than the fluorescence yield.....	454
A. The emitted intensity.....	454
B. The measured quantity.....	456
IV. The quantitative aspects of fluorescence quenching.....	457
A. The measurement of quenching constants.....	457
B. The mechanism of the quenching of fluorescence.....	460
C. The interpretation of quenching data.....	464
V. Quantitative aspects of fluorescence stabilization.....	467
A. First-order deactivation of the potentially fluorescent molecule.....	467
B. The collisional transfer of vibrational energy.....	470
VI. References.....	474

I. INTRODUCTION

The absorption of ultraviolet or visible radiation produces a transition from the ground state to a higher electronic level of a molecule. This process is usually accompanied by changes in the molecular vibrational (and rotational) energy and is represented by AB in figure 1, in which potential energy curves are drawn for the two lowest electronic states of a diatomic molecule.

The metastable excited molecule may lose its electronic energy by the emission of resonance radiation BA or of fluorescence CD after a period of 10^{-8} – 10^{-9} sec., by collisional deactivation which may lead to chemical change within this period, by undergoing a radiationless transition at some point G to a second excited state which then dissociates, or, if the absorbed quantum is of sufficient energy, i.e., greater than AE , the excited molecule may dissociate directly into atoms at J . Moreover, if the potential energy curves for the ground and excited states cross at any point, the excited molecule may undergo a radiationless transition to the corresponding vibrational level of the ground state.

Emission of fluorescence follows the collisional removal of the excess vibra-

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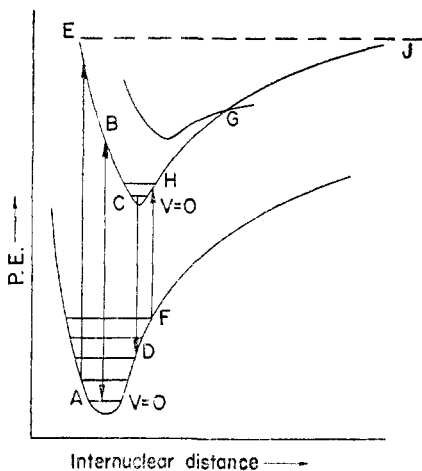


FIG. 1

FIG. 1. Potential energy curves for the ground and fluorescent states of a diatomic molecule.

FIG. 2. The temperature dependence of anti-Stokes fluorescence intensity exhibited by β -naphthylamine at 3660 Å. (56).

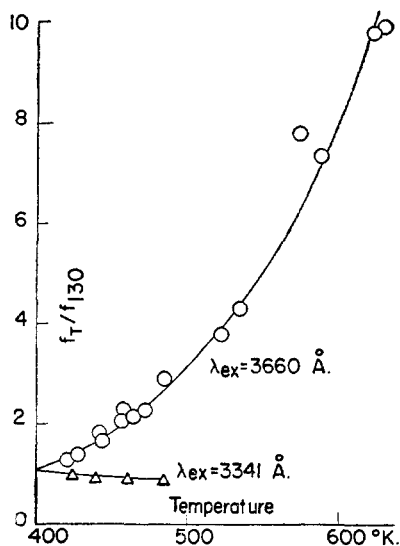


FIG. 2

tional energy BC of the excited molecule within its lifetime and is associated with transitions from its lowest vibrational level C (14); thus the fluorescence spectrum is independent of the absorbed frequency within certain limits, and under normal conditions a Stokes emission of lower energy than that of the absorbed quantum is observed. At higher temperatures of the vapor a smaller absorbed quantum may be supplemented by additional vibrational energy AF of the ground state (figure 1), in which case the fluorescence is of greater energy than absorbed, FH , and is referred to as anti-Stokes.

At very low vapor pressures such that the excited molecule undergoes no collision, its excess vibrational energy is not removed and a resonance emission is observed which is associated with transitions from the initially formed level B , and which is therefore dependent on the frequency of absorbed radiation (111).

The term fluorescence "quenching" is here defined as the collisional deactivation of the potentially fluorescent state of the molecule; if this is effected by unexcited molecules of the same species the process is referred to as "self-quenching." In the simplest case in which absorption is followed either by the quenching of fluorescence or by the emission of fluorescence, the ratio of the fluorescence intensity (f_0) emitted by a certain volume of vapor to that (f) emitted by the same volume of vapor in the presence of quenching gas at concentration $[Q]$, other conditions being the same, is given by expression I,

$$\frac{f_0}{f} = \frac{1}{\gamma} = 1 + \frac{k_q}{k_f} [Q] = 1 + K_q [Q] \quad (I)$$

where γ is the quantum yield of fluorescence in the presence of quenching gas, k_q and k_f are the rate constants of the second-order quenching and first-order emission processes, respectively, and K_Q is the quenching constant of gas Q. If z is the quenching collision frequency and p the probability of quenching on collision, expression I becomes

$$f_0/f = 1 + p\tau_0z \quad (\text{II})$$

where τ_0 , the unperturbed lifetime of the fluorescent molecule, is related to the emission probability k_f by

$$\tau_0 = 1/k_f \quad (\text{III})$$

Thus fluorescence-quenching measurements may be used to determine the rates of very fast quenching reactions, provided τ_0 can be determined independently; alternatively τ_0 may be estimated if reasonable assumptions are made concerning z and particularly p . Expression II was first used by Stern and Volmer (87) to obtain the lifetime of the excited iodine molecule from self-quenching data (110).

Excited atoms and simple molecules are very susceptible to collisional deactivation either by foreign gas molecules or by molecules of their own species; thus 0.2 mm. of hydrogen is sufficient to reduce the intensity of resonance emission of mercury vapor by 50 per cent (95), whilst at a pressure of 0.078 mm. the fluorescence intensity per iodine molecule is reduced to one-half its extrapolated value at zero concentration (110). The excited states of certain complex molecules, on the other hand, are found to be particularly resistant to collisional quenching, so that their fluorescence is observed even in solution where the excited molecule suffers some 10^5 collisions with solvent molecules during its lifetime. The chief classes of such fluorescent species are (14): (a) The ions and complexes of transition elements in which outer electron shells protect excited inner electrons from collisional perturbation; the fluorescence of this class has not been observed in the vapor phase. (b) Organic molecules containing conjugated systems of π -electrons, the excitation of which has little effect on molecular structure and stability. These compounds are fluorescent in both condensed and vapor phases and form the subject of this review. It has been proposed (27) that a condition for the observation of vapor fluorescence at moderate pressures is that two or more canonical structures may be written for the molecule in its ground state; this suggests that the excited electron is delocalized.

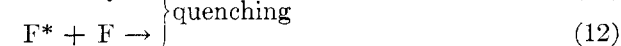
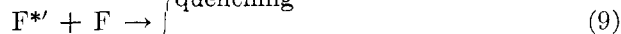
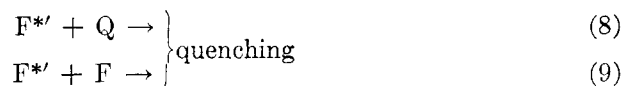
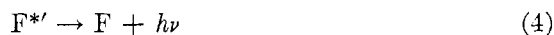
The optical behavior of simple molecules has been well established from the analysis of their discrete spectra. In the case of complex organic vapors the fewer characteristics of their continuous spectra exclude the standard methods of structural analysis and necessitate the use of photometric methods (59). It is for this reason, together with the commercial exploitation of the photoelectric effect, the necessity of pure samples, and a knowledge of their vapor pressures, that the quantitative investigation of the luminescence of organic vapors is comparatively recent. It is significant that in a discussion held in 1939 (27) on the "Fluorescence and Photochemical Kinetics of Polyatomic Molecules in the Gas Phase" only nitrogen dioxide and acetone were cited as examples.

The quenching of fluorescence in solution has been reviewed (14, 76), and

comparisons of quenching data obtained in the vapor phase and in solution have been made (16, 23) which provide information on the nature of diffusion-controlled processes in the liquid phase (54, 65). In the gas phase the collision rate can be carefully controlled, and this, together with the possibility of dissociation as a process competing with the emission of fluorescence, enables vibrational energy transfer to be investigated from the stabilization of fluorescence. Since this collisional transfer involves one particular aspect of the general photokinetic scheme, this review is written in an attempt to place this aspect in perspective with regard to the scheme as a whole.

II. THE GENERAL PHOTOKINETIC SCHEME

As the complexity of a fluorescent molecule increases, processes other than those of the simple Stern–Volmer scheme become important, so that although the quenching of fluorescence may be expressed by equation I, the measured quenching constants are not necessarily the ratio of second-order deactivation to first-order emission rate constants. Some theoretical cases have been examined by Henriques and Noyes (27), who point out that a study of the effects of several variables on the intensity of fluorescence will frequently give much information concerning the photokinetic processes taking place; the most probable of these are tabulated and discussed below.



In this scheme F, Q, and X refer to molecules of the fluorescent species, quenching gas, and inert (nonquenching) gas, respectively; the lowest excited singlet state responsible for fluorescence emission (35) is designated by an asterisk, whilst the prime denotes a molecule with vibrational energy in excess of that corresponding to thermal equilibrium. 3F refers to the lowest triplet state of F.

A. EXCITATION: PROCESS 1

Excitation is effected by absorption in the visible or near ultraviolet region of the spectrum resulting in a $\pi \rightarrow \pi^*$ transition. Since the fluorescence emission is, except in anti-Stokes fluorescence, of lower energy than that of the absorbed quantum, it is apparent that the absorption product $F^{*'}$ is a higher vibrational level of the potentially fluorescent state F^* (14).

The electronic spectra of complex organic molecules consist of several bands associated with transitions to higher electronic levels (41) which may be written



It is found, however, that regardless of the electronic level excited, the resultant fluorescence emission lies in the same spectral region as that produced by absorption in the first ultraviolet band; this evidence is summarized in Kasha's rule (35) that the emitting level of a given multiplicity is the lowest excited level of that multiplicity. Thus reaction 1a when it occurs must be followed by reaction 1b.



Examples of this "cascade" process which may involve several electronic levels, as in tesla-luminescence (2, 3) and scintillation counters (9, 11), are found in β -naphthylamine (56) and in anthracene (52, 77). In the latter case the vapor fluorescence spectrum extending from 3590 Å. to 4300 Å. is excited by absorption in both the 2500 Å. and 3660 Å. regions, with the shorter wavelength producing a broad emission continuum of higher intensity owing to the much larger absorption coefficient at 2500 Å. Luckey, Duncan, and Noyes (49) observed that the short-wave end of the fluorescence spectrum of acetone vapor lies at 26,000 cm^{-1} , whilst the lowest frequency band in absorption is near 30,800 cm^{-1} ; this indicates that emission and absorption are associated with different excited electronic levels.

The excitation of anti-Stokes fluorescence may be written



where $h\nu''$ represents a lower energy quantum than that, $h\nu'$, emitted in process 10. The complete fluorescence spectrum of aniline vapor extending from 2800 Å. to 3400 Å. has been observed with small intensity at a vapor temperature of 200°C. with an exciting wavelength of 3900 Å. (73). This large energy deficit in the absorbed quantum is unusual however, and in view of the fact that the absorption spectrum of the vapor does not extend to 3900 Å. even at 200°C., the observation should be repeated before a quantitative explanation is sought. In the case of β -naphthylamine, the vapor fluorescence spectrum extending from 3400 Å. to 4500 Å. is excited by the 3660 Å. line at 130°C. (56). Neporent does not consider this to be a true case of anti-Stokes excitation, yet under these conditions the fluorescence intensity f increases with the vapor temperature T as shown in figure 2. From the linear variation of $\log(f_T/f_{130^\circ})$ with $1/T$ (figure 3) it is concluded that the energy of the absorbed quantum (3660 Å.) is some 1900

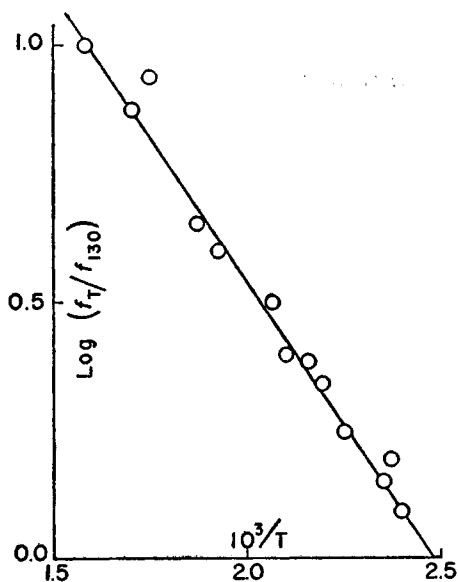


FIG. 3

FIG. 3. Logarithmic-reciprocal plot of data in figure 2

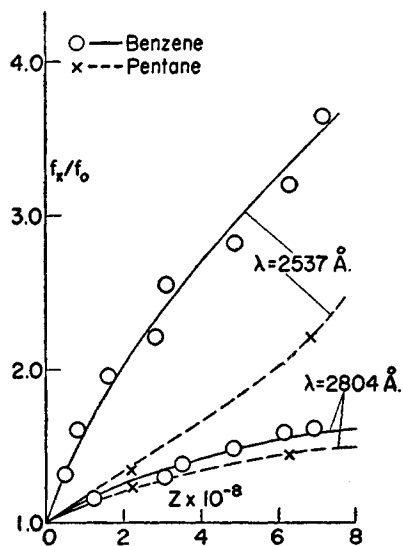


FIG. 4

FIG. 4. Fluorescence of β -naphthylamine sensitized by benzene vapor at 2537 Å. compared with typical fluorescence stabilization curve of *n*-pentane (57).

cm.^{-1} less than the energy difference between the lowest vibrational levels of the ground and excited electronic states of the molecule, which is consequently taken as $29,200 \text{ cm.}^{-1}$; this is a useful method for determining the $O' - O''$ band in those cases where both absorption and emission spectra are continuous. At 300°C . part of the fluorescence spectrum of β -naphthylamine in the region $3600\text{--}4500 \text{ \AA}$. is weakly excited by the 4047 \AA . line, and the positive temperature coefficient of the anti-Stokes fluorescence yield has recently been reported for the vapors of 3-amino-, 3,6-diamino-, and 3,6-tetramethyldiaminophthalimide (62).

Electronic excitation may also be effected by energy transfer from a second absorbing species *S*. This phenomenon of sensitized fluorescence, well known in the solid phase and in solution, may be written:



It has been observed for the vapors of acridine, acridonimine, certain phthalimide derivatives, and indigo blue with naphthalene as the sensitizing molecule *S* in each case (98, 99). Sensitized fluorescence of the relatively nonvolatile complexes aluminum 8-quinolinolate and magnesium phthalocyanine has been observed where direct excitation failed (99), and the large enhancement of the fluorescence of β -naphthylamine excited by the 2537 \AA . line on the addition of benzene vapor (shown in figure 4) is attributed to this effect (57). The observation of an anti-Stokes sensitization of the fluorescence of aniline vapor by indigo at 3900 \AA . and of the fluorescence of benzene vapor by aniline at 2800 \AA . (73, 75)

indicates that it is not a necessary condition for sensitization that the sensitizing species should absorb at shorter wavelengths than the emitting molecule.

The tesla-luminescence of benzene vapor has been observed (2, 3), and the excitation of fluorescence by α -particles, x-rays, and γ -radiation is well known in connection with scintillation counters. This review is confined to the processes following the absorption of visible or near ultraviolet radiation.

B. FIRST-ORDER DEACTIVATION OF THE ABSORPTION
PRODUCT: PROCESSES 2 TO 4

1. *Dissociation*

When the energy of the quantum absorbed by a diatomic molecule reaches a critical value, the probability of direct or predissociation increases from zero to a value some several hundred times greater than the probability of emission, fluorescence is no longer observed, the lifetime of the excited molecule decreases sharply, and the absorption spectrum becomes diffuse or continuous (55). Thus in this case dissociation and the emission of fluorescence are mutually exclusive processes.

Of the large number of vibrational modes of a complex molecule, those which are totally symmetric are most strongly excited in an electronic transition; since these would lead to the simultaneous disruption of more than one bond, it is concluded (85) that nontotally symmetric vibrations must be largely responsible for the dissociation of these highly symmetrical molecules. Thus process 2 consists of the stages



where the subscript denotes an excess of vibrational energy in nontotally symmetric modes. The coupling of totally symmetric with nontotally symmetric vibrations represented by process 2a is brought about by anharmonic forces which increase with the amplitude and energy of the optically excited vibrations. The time required for this internal redistribution of vibrational energy to take place may be of the order of the decay time, in which case fluorescence emission and photodissociation are competing processes over a wide range of absorbed frequencies, with the latter becoming increasingly predominant as this frequency is increased (55, 56).

An increase in the temperature of the vapor excites both symmetric and non-symmetric vibrations in the ground state. According to the selection rules the excited nonsymmetric vibrations are preserved during the electronic transition so that the production of F_{ν}^* according to process 2c



becomes important at higher temperatures (56, 85).

Thus the overall probability of process 2 increases with the total vibrational energy reserve of the molecule which may be excited both optically and thermally

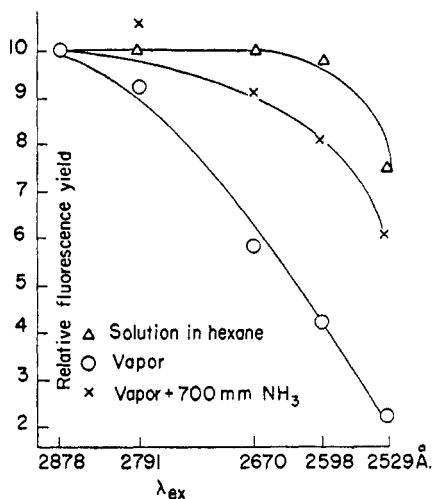


FIG. 5

FIG. 5. Variation of fluorescence yield of aniline with wavelength of absorbed radiation (100).

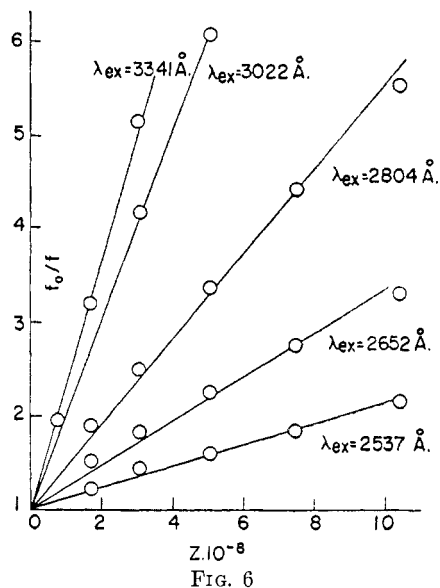
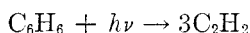


FIG. 6

FIG. 6. Quenching of fluorescence of β -naphthylamine by oxygen at various wavelengths of absorbed radiation (56).

(56, 85). This is manifest in the reduction in the fluorescence efficiency of acetaldehyde (80), acetone (25, 64), aniline (55, 103) (shown in figure 5), β -naphthylamine (56), and certain phthalimide derivatives (61) as the frequency of the absorbed radiation is increased, and the reduced fluorescence efficiency of acetaldehyde (80), aniline (100, 103, 104), β -naphthylamine (56), and the same phthalimides (61) (see table 1) at higher vapor temperatures. Moreover, direct measurements of the quantum yield of dissociation of acetone by the 3130 Å. line show that this approaches unity at temperatures slightly above 100°C. (66).

It is unfortunate that the search for photoproducts obtained during the excitation and measurement of fluorescence has been conducted in so few cases. However, it has been shown (55, 103, 104) that absorption in the region 2800–2500 Å. results in the rupture of the carbon–nitrogen bond in aniline, whilst at shorter wavelengths the aromatic properties of the molecule are destroyed. A similar variation in the mode of disruption with absorbed frequency has been reported in the case of benzene (42, 74), and the production of ethylene in the region 1855–2000 Å. has led Wilson and Noyes (109) to propose the primary process



for which a symmetric vibration would appear responsible. Following a quantitative treatment of the data for β -naphthylamine it has been suggested (92) that both the mechanism and the rate of the first-order radiationless transition depend on the vibrational energy reserve of the electronically excited molecule; however, there is no direct evidence that either of these deactivation processes involves

TABLE 1
Fluorescence yields (γ) of some phthalimide derivatives in the vapor phase (61)

Molecule	Concentration	λ_{ex}	T	γ
	<i>molecules/cc.</i>	\AA .	$^{\circ}\text{C}$.	
3,6-Diaminophthalimide.....	$0.1-2.0 \times 10^{16}$	3850	216	0.014
			265	0.008
			316	0.0045
3-Dimethylamino-6-aminophthalimide...	$0.1-1.0 \times 10^{16}$	4360	265	0.59
			305	0.52
			355	0.50
3,6-Tetramethyldiaminophthalimide....	1.0×10^{16}	5200	243	0.60
			284	0.46
			335	0.30

dissociation. The relationship of the primary photodissociation process to the emission of fluorescence has been investigated in the case of acetone (48) and biacetyl (82), and has recently been discussed for simple ketones in general (67).

The reduction in the lifetime of the potentially fluorescent molecule owing to process 2 accounts for the observed parallel reduction in the quenching of the fluorescence of aniline by oxygen (55) and the quenching of the fluorescence of β -naphthylamine by oxygen (56) and carbon tetrachloride (22) as the absorbed frequency is increased, according to expression II; the quenching of the fluorescence of β -naphthylamine by oxygen has a negative temperature coefficient for the same reason (56). Figure 6 shows the effect of absorbed frequency on the quenching of the fluorescence of β -naphthylamine by oxygen.

In the case of diatomic molecules, photodissociation can be detected from the diffuse or continuous appearance of their absorption spectra. Owing to the larger number of vibrational modes and closely spaced rotational levels of polyatomic molecules however, their absorption spectra often have a continuous appearance throughout the whole absorption range, and the excitation of fluorescence with high efficiency in some cases (56, 90) indicates that the appearance of an absorption continuum is not an unambiguous criterion for the onset of dissociation (55, 63). Nevertheless the observation of both discrete and continuous regions in absorption has been taken as evidence for dissociation in the latter region in the cases of acetaldehyde (80), acetone (64), aniline (100), naphthalene (108), and benzaldehyde (96).

The conditions for predissociation of polyatomic molecules have been discussed by Spomer and Teller (85), who point out that the phenomenon is more frequently observed than for diatomic molecules, and that the associated diffuse region in absorption may extend over several 100 \AA . where dissociation and emission are competing processes. In this case the predissociating state is a different vibrational level of the fluorescent state.

2. Internal conversion

If, in the absence of quenching, the fluorescence yield is found to be less than unity under conditions where process 2 is nonoperative (i.e., in solution (1, 19)

or at long wavelengths), this must be due to either process 3a or process 3b or both.



Until recent years process 3a was the only recognized alternative, and measurements of the increase in temperature of fluorescent solutions due to this process have been used to obtain fluorescence efficiencies in the dissolved phase (1) which are in good agreement with values obtained directly (17, 19).

However, since the classic work of Lewis and Kasha (44, 45) confirmed previous suggestions (46, 97) associating the well-known phosphorescence of these molecules in rigid media with the lowest triplet state 3F , the importance of the spin intercombination process 3b has been recognized. Owing to the relatively long lifetime of ca. 10^{-4} sec. (72) of the triplet state and its chemical reactivity as a biradical (44), phosphorescence has so far been observed only for the vapors of biacetyl and possibly acetone (38, 45) following ultraviolet absorption, and for acetaldehyde, benzaldehyde, and acetophenone excited by an electrodeless discharge at high pressures (78). However, triplet \rightarrow triplet absorption spectra have been measured for a number of complex fluorescent vapors, using the flash technique to obtain the necessary high initial concentration of excited molecules (72), and the fact that the probability of the singlet \rightarrow triplet transition is independent of gas pressure, except possibly at lower pressures, indicates that the process is first order as written.

It has been suggested that one of the two unimolecular deactivations undergone by the excited β -naphthylamine molecule is a spin intercombination process of this type (92); this reduces the fluorescence yield as does dissociation and, apart from the absorption method mentioned above, these processes can only be distinguished by a search for disintegration products, the importance of which is again emphasized.

The evidence indicates that process 3b has a much higher probability than process 3a (35, 37) and is greatly influenced by the presence of heavy or paramagnetic atoms in the molecule (34, 35, 112). Thus, whilst the fluorescence spectra of benzene, fluorobenzene, toluene, benzonitrile, aniline, and benzaldehyde have been obtained (5, 6, 24, 96, 102), substitution of the heavier chlorine atom in the benzene molecule increases the probability of process 3b to such an extent that fluorescence is no longer observed (6).

If the triplet level undergoes a radiationless transition to the singlet ground state (51, 71, 72), as in process 3c, the absorbed quantum appears entirely as



thermal energy (1) and the overall result is that of process 3a.

One further consequence of process 3b is the absence of fluorescence following the weaker $\eta \rightarrow \pi$ transition in nitro compounds, quinones, and simple heterocyclic molecules. The longer-lived $\eta\pi^*$ state undergoes a virtually complete conversion to the triplet level and the phosphorescence yield of these compounds in rigid solvents is close to unity at low temperatures (7, 35).

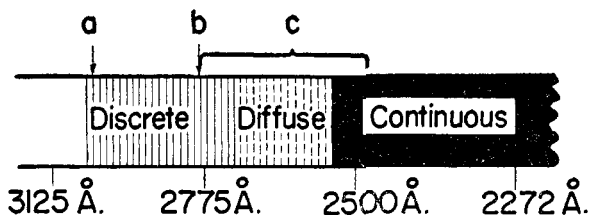


FIG. 7. Schematic representation of absorption spectrum of aniline vapor at low pressures (100).

For further information on the widespread significance of spin intercombinations the reader is referred to the timely and comprehensive review by Kasha and McGlynn (37).²

3. Resonance emission

Process 4 represents the "resonance" emission observed in the case of benzene (40), aniline (102), and naphthalene (81) at very low pressures. Under these conditions the absorption product F^{*} undergoes no collision and emission occurs before thermal equilibrium of the excited molecule is established. The normal fluorescence is restored, however, if (a) the vapor pressure is increased (24, 40, 102), (b) inert gases are added (24, 81, 102), (c) the temperature is raised (81, 102), or (d) the energy of the absorbed quantum is increased (102, 108). Circumstances (a) and (b) increase the collision rate, and the excess vibrational energy of F^{*} undergoes an intermolecular redistribution as in the case of diatomic molecules; this is not so in cases (c) and (d). The vibrational energy excited in symmetrical modes reappears in the resonance spectrum as for the diatomic molecule, but if this is sufficiently large it can be internally redistributed amongst nonsymmetrical modes according to process 2a before fluorescence emission takes place as discussed above. The excited molecule can then emit if the vibrational energy is insufficient to cause dissociation and the vibrational energy will not contribute to the emitted quantum so that the normal fluorescence spectrum is observed. This emission may be written



The intramolecular redistribution of excess vibrational energy of the excited molecule, process 2a, represents a fundamental difference in characteristic between a polyatomic and a diatomic molecule (55). Its probability W depends not only on the reserve of vibrational energy but also on the complexity of the molecule (59); thus the fluorescence spectrum of anthracene vapor remains unchanged (apart from reabsorption effects) even at the lowest pressures (77), indicating that process 2a is completed with the lifetime of the excited state. Neporent (59) has defined a complex fluorescent molecule as one for which $W > 1/\tau_0$, but owing to its energy dependence, W is not a well-defined molecular characteristic; a further subdivision of "complex" molecules has been proposed

² The author is very grateful to Professor Kasha for providing a copy of this review prior to its publication.

depending on the magnitude of vibrational and electronic interaction as reflected in the characteristics of both absorption and emission spectra (60). The delicacy of the resonance spectrum can be visualized in the case of aniline, which has the typical absorption spectrum shown in figure 7. At low pressures (0.02 mm.) and room temperature, monochromatic absorption in the region *ab* produces a resonance progression of sharp bands; excitation beyond point *b*, although still in the discrete region of absorption, results in the appearance of normal (continuous) fluorescence. The increase in the absorbed quantum is 5 kcal./mole (100).

C. SECOND-ORDER DEACTIVATION OF THE ABSORPTION PRODUCT: PROCESSES 5 TO 9

1. The establishment of thermal equilibrium

Under conditions such that emission and dissociation are competitive processes it is found that the addition of inert (nonquenching) gases increases the overall fluorescence yield (55, 56, 100). This is attributed to the stabilization of the excited molecule by collisional removal of its excess vibrational energy (process 5), thus reducing the dissociation probability. Figure 5 illustrates the stabilization of the fluorescence of aniline vapor by the addition of ammonia (100), and the relative intensification of the fluorescence of aniline and β -naphthylamine as a function of inert gas pressure is shown at different exciting wavelengths in figures 8 and 9. The effect has also been observed in the case of benzene (55).

A recent interesting observation that inert gases *quench* the anti-Stokes

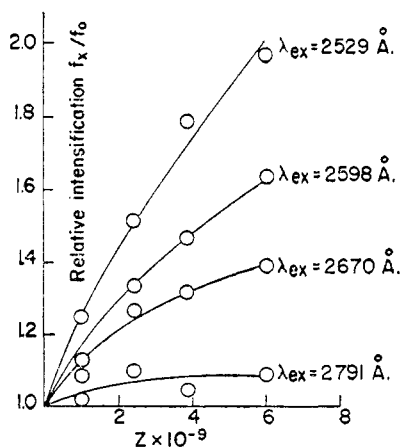


FIG. 8

FIG. 8. Intensification of fluorescence of aniline vapor by inert gas (ethylene) at different wavelengths (55).

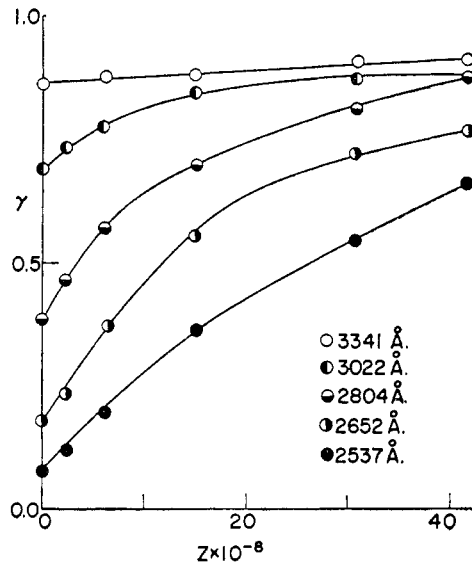


FIG. 9

FIG. 9. Effect of inert gas (pentane) on fluorescence yield of β -naphthylamine vapor (57).

fluorescence of 3,6-tetramethyldiaminophthalimide at low pressures is explained in terms of vibrational energy transfer in the reverse direction (12). The lowest vibrational levels of the fluorescent state formed on absorption have less energy than that corresponding to thermal equilibrium which is restored by collision with the inert gas; the increase in the vibrational energy reserve results in a corresponding increase in the rate of dissociation. This process may be written thus:



Collisional stabilization increases the lifetime of the fluorescent molecule; this accounts for the increase in measured quenching constant found when ethane and cyclohexane are added to β -naphthylamine quenched by carbon tetrachloride vapor (22). The "flare-up" of luminescence exhibited by the unquenched alpha and poly derivatives of anthraquinone in the presence of nitric oxide is attributed to a similar inhibition of spontaneous dissociation by transfer of the excess vibrational energy of the fluorescent molecule to the foreign gas (33). The very large increase in intensity in this case, however, is probably due to the photochemical production of a second emitting species with a more intense fluorescence in the measured region.

Inert gas molecules in this way remove any dependence of vapor fluorescence on the frequency of the incident radiation, much as solvent molecules in solution do (22). That stabilization by unexcited fluor molecules takes place is evidenced in the change from resonance emission to fluorescence emission of both benzene (24, 40) and aniline (102) as the vapor concentration is increased. This effect, written as process 6, is also produced by inert gases at higher pressures (24, 102), indicating a larger stabilizing efficiency of the "parent" molecule.

There is no apparent reason why quenching molecules should not also behave as inert gases in this respect, and in at least one case process 7 has been accorded a high probability (22). However, it has been observed that oxygen, unlike inert gases, does not cause a redistribution of line intensities in the discrete emission spectrum of aniline at low pressures, but quenches evenly the entire spectrum (102); this suggests that every collision between aniline and oxygen results in quenching.

2. *Electronic deactivation*

The quenching process 8 and 9 must involve the absorption product in view of the immediately preceding remarks. The nature of the quenching process is discussed later.

D. FLUORESCENCE EMISSION: PROCESS 10

By analogy with the behavior of diatomic molecules, emission of fluorescence is associated with transitions from the lowest vibrational level of the first singlet excited state to the various vibrational levels of the ground state (14). This accounts for the fact that the fluorescence spectrum is independent of the magnitude of the absorbed quantum. It is probably more accurate to associate the

fluorescence spectrum with transitions from the spontaneous or collision-induced equilibrium population of totally symmetric vibrations in the upper state (91). With the exception of azulene, where a higher excited singlet state is responsible (8, 105), the fluorescent level is in all cases the lowest excited singlet state of the molecule (35), and emission of fluorescence is shown as process 10. In no case has emission of fluorescence been observed from more than one electronic state of the same molecule, although Birks (11) has proposed that the cascade process 1b in anthracene is due to reabsorption of the very fast emission from the higher singlet state produced by absorption at 2500 Å. to form ultimately the lowest excited singlet state which emits the normal fluorescence spectrum. Emission from two excited states of the acetone molecule has been observed (48), but one of these with a lifetime of 10^{-4} sec. has been shown to be the triplet state associated with emission of phosphorescence (38).

If a molecule contains more than one electronic system, as in a substituted aromatic hydrocarbon, each system may absorb independently of the other. Thus the discrete absorption spectrum of aniline in the region 2632–2980 Å. has a band spacing characteristic of the phenyl group (102). In the range 2100–2400 Å. absorption is continuous, with a maximum attributed to the amino group (29); excitation in the latter region produces no vapor fluorescence owing to the high decomposition probability, but absorption in both regions excites the same fluorescence spectrum in solution (55, 100). Some internal transfer of electronic energy must therefore follow excitation of the amino group. In the case of benzaldehyde vapor, Terenin concludes that absorption by the benzene ring excites emission by the carbonyl group (96).

Emission of fluorescence follows the laws of exponential decay and, like the phenomenon of radioactivity, its half-life in the absence of perturbation is insensitive to changes in temperature or pressure and is the same in rigid or fluid media. The emission probability provides the yardstick with which the rates of competing processes may be measured, and it has been suggested (10) that the lifetime τ_0 of the unperturbed molecule has the value of 3.5×10^{-9} sec. for all aromatic hydrocarbons. Until this is confirmed, however, τ_0 must be determined for each molecule before a quantitative interpretation of experimental data is made.

E. SECOND-ORDER DEACTIVATION OF THE FLUORESCENT LEVEL: PROCESSES 11 AND 12

The quenching of fluorescence by foreign gases is found to be specific (22, 55, 56, 90, 102). Oxygen and nitric oxide are the most efficient quenching species, but in those cases where self-quenching has been investigated the unexcited fluorescent molecule is equally potent (90).

The quenching of sensitized fluorescence by oxygen has been observed in mixtures of acridine and naphthalene vapors at 2790 Å.; since pure acridine is unquenched, it must be concluded that oxygen deactivates the sensitizing naphthalene molecule (98).

The mechanism of the quenching process is discussed later.

F. THE OVERALL FLUORESCENCE YIELD

The available evidence suggests that processes 2 to 12 are the most probable ones following the electronic excitation of a complex fluorescent molecule in the vapor phase. The intensity of incident radiation is normally such that even under conditions of complete absorption, the photostationary concentration of excited molecules is negligibly small compared with the total fluor concentration; for this reason second-order processes involving two excited molecules, as well as the effects of dissociation products, may be neglected.

If k_n is the rate constant of process n , then under photostationary conditions when

$$d[F^*]/dt = d[F^*]/dt = 0$$

the total intensity f of fluorescence is given by

$$f = k_4[F^*] + k_{10}[F^*] \quad (\text{IV})$$

and the overall fluorescence yield γ for the above scheme is related by

$$\gamma = \frac{f}{I_a} = \left\{ \frac{1}{k_2 + k_3 + k_4 + k_5[X] + k_6[F] + k_7[Q] + k_8[Q] + k_9[F]} \right\} \\ \times \left\{ k_4 + k_{10} \left(\frac{k_5[X] + k_6[F] + k_7[Q]}{k_{10} + k_{11}[Q] + k_{12}[F]} \right) \right\} \quad (\text{V})$$

where I_a , the intensity of absorbed radiation, is equal to the rate of formation of excited molecules.

Expression V may be simplified by the assumption that the fluorescence decay time is independent of the vibrational level of the fluorescent state, i.e., that $k_4 = k_{10}$. This is perfectly reasonable in view of the fact that processes 4 and 10 concern radiative transitions between the same electronic states. In this case expression V becomes

$$\frac{1}{\gamma} = \left\{ 1 + \frac{k_{11}[Q]}{k_{10}} + \frac{k_{12}[F]}{k_{10}} \right\} \\ \times \left\{ \frac{k_2 + k_3 + k_{10} + k_5[X] + k_6[F] + k_7[Q] + k_8[Q] + k_9[F]}{k_5[X] + k_6[F] + k_7[Q] + k_{10} + k_{11}[Q] + k_{12}[F]} \right\} \quad (\text{VI})$$

It will further be assumed at this stage that the rate of collisional quenching is also independent of the vibrational level of the potentially fluorescent molecule, i.e., $k_8 = k_{11}$ and $k_9 = k_{12}$. This reduces expression VI to

$$\frac{1}{\gamma} = \left\{ 1 + \frac{k_{11}[Q]}{k_{10}} + \frac{k_{12}[F]}{k_{10}} \right\} \\ \times \left\{ 1 + \frac{k_2 + k_3}{k_5[X] + k_6[F] + k_7[Q] + k_{10} + k_{11}[Q] + k_{12}[F]} \right\} \quad (\text{VII})$$

Thus the measurement of γ under varying conditions can provide information concerning the rate constants of processes 2 to 12. As the number of constants

exceeds the number of variables however, the estimation of a particular rate constant may require the introduction of certain assumptions concerning some of the others, and although the scheme constructed above is useful in predicting the behavior of an excited complex molecule in the vapor phase, each has its peculiar characteristics which must be examined individually.

III. THE DEPENDENCE OF INTENSITY OF FLUORESCENCE ON FACTORS OTHER THAN THE FLUORESCENCE YIELD

The fluorescence yield γ is defined as the ratio of the number of quanta emitted per second to the number of quanta absorbed per second by the same quantity of material. Since the fluorescence radiation is emitted over a relatively wide frequency range in all directions, its total intensity and hence the fluorescence yield is a difficult quantity to determine accurately. In practice a certain frequency range of the emission is measured along one direction, and in order to obtain results of significance, the measuring device should determine a quantity proportional to the number of quanta emitted regardless of frequency (27). Some photoelectric cells and photomultipliers are suitable for this purpose, although their wavelength sensitivity range is relatively restricted and emission spectra must fall within certain frequency limits if they are to be measured in this way.

It is important that any change in the measured quantity should reflect a proportional change in the fluorescence yield, and since the measured intensity in almost all cases differs from the emitted intensity, the possible effects of factors other than the fluorescence yield on both these quantities will be considered briefly.

A. THE EMITTED INTENSITY

By definition the total intensity f of emitted radiation is given by

$$f = I_0[1 - \exp(-\epsilon cd)] \times \gamma \quad (\text{VIII})$$

where I_0 is the intensity of the incident beam, and ϵ , c , and d are the absorption coefficient, concentration, and absorption path of the fluorescent vapor, respectively. f will be determined by the following factors.

1. *The intensity of incident radiation*

For a given volume of gas f is directly proportional to I_0 , which must therefore remain constant during a series of related measurements. If the incident intensity is very large however, so that the concentration of excited molecules at any time is appreciable (as in flash photolysis), then second-order processes involving two of these become important and a dependence of γ on I_0 may be expected.

2. *The frequency of incident radiation*

Since the absorption coefficient ϵ varies considerably with the incident frequency, the latter determines the rate of formation of excited molecules and hence the fluorescence intensity f . It is desirable that the incident radiation be

monochromatic, so that the energy of the absorption product is kept within narrow limits and its value can be reliably estimated.

3. *The temperature of the vapor*

The temperature of the vapor controls the population of vibrational levels in the ground state of the absorbing molecule and any variation will affect the absorption coefficient at a particular wavelength, as in the case of acetone (48) and β -naphthylamine (56). Absorption measurements should therefore be an integral part of any investigation of the temperature coefficient of γ . The temperature coefficient of the vapor concentration c will depend on the method employed for its control.

4. *The concentration of fluorescent vapor*

The rate of production of excited molecules is determined by the vapor concentration c , which must be taken into account when this is the variable quantity (79, 90). At low concentrations f is directly proportional to c provided ϵ and d are not unduly large; this fact has been exploited in the measurement of sublimation pressures from fluorescence data (89).

5. *The concentration of inert gases*

The addition of inert gases ensures the establishment of thermal equilibrium of the fluorescent molecule in both its ground and fluorescent states. At very low fluor concentrations the introduction of inert gases may shift the absorption spectrum slightly and change the absorption coefficient at the particular wavelength used for excitation. The effect has been studied quantitatively in the case of β -naphthylamine (58), where the "partial weakening" of fluorescence, owing to a parallel reduction in ϵ , increases with the pressure of helium and other light gases to a maximum at relatively low pressures, as shown in figure 10. It appears that neither the mass nor the radius of the inert gas molecule determines the magnitude of its effect, which decreases in the order $\text{He} > \text{H}_2 > \text{N}_2 > \text{NH}_3 > \text{CO}_2$ (58).

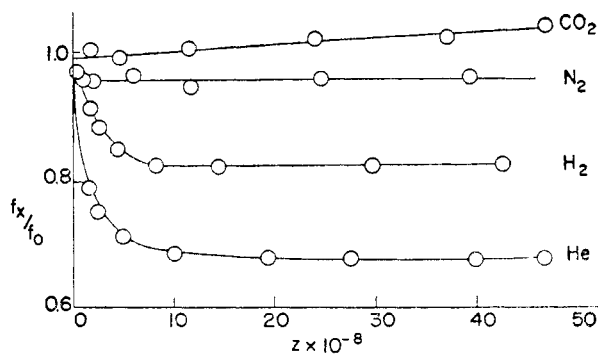


FIG. 10. "Partial weakening" of fluorescence of β -naphthylamine by foreign gases (58). $\lambda_{ex} = 3341 \text{ \AA}$.; $T = 150^\circ\text{C}$.; β -naphthylamine pressure = 0.53 mm.

A much larger weakening effect would be expected if the added gas absorbs in the region used for excitation, and the importance of absorption measurements in the interpretation of fluorescence data is emphasized.

6. The concentration of quenching gases

It is necessary to distinguish the quenching process from thermal reactions or photoreactions involving the unexcited fluorescent molecule which effectively reduce the fluor concentration. A suggested interpretation of the quenching of the fluorescence of anthracene vapor by sulfur dioxide in terms of both a thermal reaction of sulfur dioxide with the ground state and a photoreaction with the excited state of the anthracene molecule has been given (90). In this case equation I is not obeyed and the quenching molecule greatly reduces the absorbing power of the fluor.

As with inert gases, the effect of quenching gas on the rate of formation of excited fluorescent molecules should be examined in each case even if the added gas does not itself absorb in the region studied.

B. THE MEASURED QUANTITY

In practice the ratio of the intensity F of part of the fluorescence spectrum viewed in one direction to the intensity BI_0 of a reference beam monitored from the excitation source is measured; in this way errors due to fluctuations in the source are minimized. Differential photomultiplier set-ups have been described for this purpose (16, 21).

Various "optical circuits" have been designed in which the fluorescence is viewed from the front (90) or rear (79) cell surface or at an angle of 90° to the incident beam (16, 21). In each case the filter necessary to remove scattered incident radiation usually absorbs the short-wave region of the emitted spectrum.

The relationship between the measured quantity and the total fluorescence intensity f is clearly

$$F/BI_0 = Af/BI_0 = (A/B)[1 - \exp(\epsilon cd)]\gamma \quad (\text{IX})$$

where A is the fraction of fluorescent radiation intercepted by the measuring instrument. Thus if F_1/BI_0 and F_2/BI_0 are measured under conditions 1 and 2

$$\frac{(F_1/BI_0)}{(F_2/BI_0)} = \frac{f_1}{f_2} = \frac{[1 - \exp(-\epsilon_1 c_1 d)] \gamma_1}{[1 - \exp(-\epsilon_2 c_2 d)] \gamma_2} \quad (\text{X})$$

and if ϵ and c remain unchanged,

$$\frac{(F_1/BI_0)}{(F_2/BI_0)} = \frac{f_1}{f_2} = \frac{\gamma_1}{\gamma_2} \quad (\text{XI})$$

If F/BI_0 and γ are known under any given set of conditions, then γ can be calculated for any other set of conditions for which F/BI_0 is measured, and expression VII can be used to determine the relative rates of the operative photochemical processes.

It is essential that both c and ϵ remain unchanged if expression XI is to be valid for measurements made under varying conditions. Any variation in these quan-

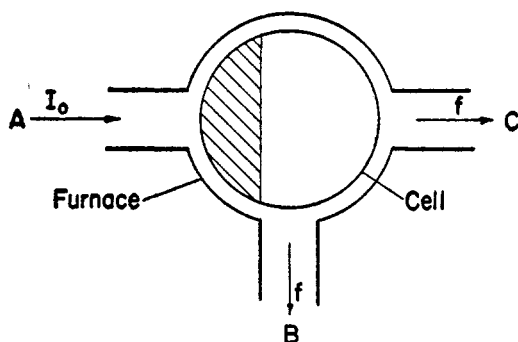


Fig. 11. Plan of typical fluorescence cell illustrating "window effect"

tities should find compensation in the use of expression X, in which respect the following points are made:

(a) Since the filters transmit only part of the fluorescence spectrum, the energy distribution of the latter must remain unchanged during a series of related measurements.

(b) If the concentration of the fluorescent vapor is the variable quantity, the optical arrangement must be such that measurements are unaffected by changes in the emission "center of gravity." At high vapor concentrations the incident radiation will be almost completely absorbed in the front (shaded area) of the cell shown in figure 11. The emission from this area will not be detected by an instrument placed at B, which will record a maximum intensity at a vapor concentration lower than that required for complete absorption (21, 52, 88). Such an arrangement is particularly unsatisfactory for the measurement of concentration effects and the recording instrument should be placed at either A or C, at a sufficient distance from the cell to minimize effects due to the change in the emission center of gravity in the direction AC (79). One disadvantage of viewing at A and C is that the strong filters necessary to remove the intense reflected or transmitted exciting beam greatly reduce the measurable fluorescence intensity.

(c) If an added gas or the fluorescent vapor itself acts as an inner filter by absorbing part or all of the fluorescence spectrum, then changes in the concentration of these molecules will produce results of little significance. The polychromatic nature of the emitted radiation makes a correction for this effect extremely difficult to apply (79), so that foreign gases which absorb in this region should not be used. Usually a fluorescent molecule does not reabsorb the long-wave portion of its emission spectrum which is transmitted by the filters and the errors in this case are not serious (90). If the added gas absorbs the monochromatic incident radiation a correction is easily made, but the kinetic scheme may be further complicated by the presence of electronically excited molecules of a foreign gas.

IV. THE QUANTITATIVE ASPECTS OF FLUORESCENCE QUENCHING

A. THE MEASUREMENT OF QUENCHING CONSTANTS

The ratios of the second-order deactivation to first-order emission rate constants, k_{11}/k_{10} and k_{12}/k_{10} , are referred to as the quenching constants K_Q and

K_F for foreign gas and self-quenching, respectively. Their determination is conveniently illustrated by reference to work on anthracene and β -naphthylamine.

1. Anthracene

Using the 3660 Å. mercury line for excitation at a temperature of 280–340°C., the fluorescence intensity of anthracene vapor has been measured at various pressures and in the presence of inert and quenching gases (90).

It was found that

- (a) The fluorescence yield, when corrected for collisional perturbation, is approximately unity; hence $k_2 = k_3 = 0$.
- (b) The inert gases hydrogen, nitrogen, argon, ethylene, and hydrogen sulfide have no effect on either the fluorescence yield or the intensity; this confirms the absence of processes 2 and 3, and eliminates process 5 and, by analogy, processes 6 and 7.
- (c) The quenching constants obtained for oxygen both in a vacuum and in the presence of 760 mm. of nitrogen are in good agreement, supporting the conclusions drawn in (a) and (b).

Thus expression VII becomes

$$\frac{f_0}{f} = \frac{\gamma_0}{\gamma} = 1 + K_Q[Q] + K_F[F] \quad (\text{XII})$$

where f_0 and γ_0 refer to the fluorescence intensity and yield, respectively, in the absence of quenching processes.

K_F was determined from the variation in fluorescence intensity with the concentration of anthracene vapor; the method of frontal illumination was used, and the expression derived (79) for self-quenching in solution, i.e., a form of expression IX was employed to allow for the increased rate of formation of excited molecules with concentration.

K_{O_2} and K_{NO} were obtained from quenching measurements at low anthracene pressures where self-quenching may be neglected and expression XII reduces to expression I. At higher concentrations of anthracene, where self-quenching is appreciable, the reduction in fluorescence intensity from f_0 to f by the introduction of quenching gas is given by expression XIII,

$$\frac{f_0}{f} = \frac{1 + K_Q[Q] + K_F[F]}{1 + K_F[F]} = 1 + K'_Q[Q] \quad (\text{XIII})$$

and since [F] remained constant, Stern-Volmer behavior was observed with oxygen and nitric oxide as quenching gases. The measured constants

$$K'_Q = K_Q/(1 + K_F[F])$$

when corrected for self-quenching according to expression XIII, agreed with K_Q obtained at low anthracene pressures and with previous values (16, 53). The quenching data for anthracene, 9-phenylanthracene, and 9, 10-diphenylanthracene are given in table 3.

2. *β -Naphthylamine*

Curme and Rollefson (22) studied the effect of the inert gases ethane and cyclohexane on the quenching by carbon tetrachloride of β -naphthylamine fluorescence excited by the lines 2537–2650 Å. and 3130 Å. Under these conditions processes 2 or 3 or both are operative (56). These authors neglected the effect of self-quenching, since this would have caused trends in the results which were not observed, and which would in any case be negligible at the low fluor concentrations used; they further assumed that the quenching gas stabilizes, but does not quench, the absorption product, which in this case may be a higher excited singlet state (22, 56). The elimination of process 8 and preference for process 7 is the reverse of the conclusions drawn from the even quenching of the aniline resonance spectrum by oxygen (102), and is unnecessary if the rate constants of processes 8 and 11 are assumed equal, as in expression VII. However, the use of expression V in this case, with k_4 assumed zero, leads to

$$\frac{1}{\gamma} = \left\{ 1 + \frac{k_{11}[\text{Q}]}{k_{10}} \right\} \left\{ \frac{k_2 + k_3 + k_5[\text{X}] + k_6[\text{F}] + k_7[\text{Q}]}{k_5[\text{X}] + k_6[\text{F}] + k_7[\text{Q}]} \right\} \quad (\text{XIV})$$

and if f_0 and γ_0 are the fluorescence intensity and yield, respectively, in the absence of quenching gas, then

$$\frac{f_0}{f} = \frac{\gamma_0}{\gamma} = (1 + K_{\text{Q}}[\text{Q}]) \left\{ \frac{k_2 + k_3 + k_5[\text{X}] + k_6[\text{F}] + k_7[\text{Q}]}{k_2 + k_3 + k_5[\text{X}] + k_6[\text{F}]} \right\} \\ \times \left\{ \frac{k_5[\text{X}] + k_6[\text{F}]}{k_5[\text{X}] + k_6[\text{F}] + k_7[\text{Q}]} \right\} \quad (\text{XV})$$

The quantity $(f_0/f - 1)/[\text{Q}]$ increases with inert gas pressure to a maximum value equal to K_{Q} as the fractions in XV containing $[\text{X}]$ approach unity; the value of 950 liters mole⁻¹ is obtained for the quenching constant at both frequencies.

Neporent (56) investigated the quenching by oxygen of the fluorescence of β -naphthylamine at very low fluor concentrations and at various temperatures, using different wavelengths of exciting radiation. Under these conditions second-order processes involving F may be ignored, and in the absence of inert gases stabilization of the absorption product does not take place if, as Neporent justifiably but tacitly assumed, process 7 is negligible. Expression VII is reduced under these conditions to

$$\frac{1}{\gamma} = \left\{ 1 + \frac{k_{11}[\text{Q}]}{k_{10}} \right\} \left\{ 1 + \frac{k_2 + k_3}{k_{10} + k_{11}[\text{Q}]} \right\} \quad (\text{XVI})$$

and the quenching is expressed by

$$\frac{f_0}{f} = \frac{\gamma_0}{\gamma} = 1 + \frac{k_{11}[\text{Q}]}{k_2 + k_3 + k_{10}} = 1 + K'_{\text{Q}}[\text{Q}] \quad (\text{XVII})$$

The measured quenching constant K'_{Q} was found to decrease as either the temperature or the exciting frequency increased, owing to the dependence of processes 2 and 3 on the vibrational energy reserve of the molecule. However, the Stern-

Volmer plots shown in figure 6 are obtained at constant temperature. Neporent translated his quenching data directly into lifetime values as discussed below in Section V,A, but at 3660 Å. and 130°C., under which conditions processes 2 and 3 do not take place, K_Q is calculated to be 3800 liters mole⁻¹. That this is some four times greater than the quenching constant for carbon tetrachloride is attributed to the higher collision frequency and efficiency of the faster paramagnetic oxygen molecule. (See Section IV,B below.)

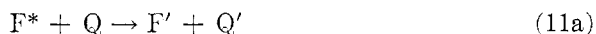
B. THE MECHANISM OF THE QUENCHING OF FLUORESCENCE

The term "quenching" is usually applied to any process which lowers the fluorescence yield. Thus internal, collisional and inner-filter, compound or "static" quenching have been recognized in solution (14, 16), and thermal quenching in the vapor phase has been used to describe process 2 (100). Here the term will be restricted to the second-order deactivation of the potentially fluorescent molecule; this process appears to be specific and the effect of quenching molecules will be discussed according to their magnetic properties.

1. Paramagnetic quenching molecules

The high efficiency of the paramagnetic molecules oxygen and nitric oxide in quenching the fluorescence of aromatic compounds in the adsorbed (32, 33, 39, 84), dissolved (15, 16, 17, 106, 107), and vapor (16, 26, 31, 55, 56, 90, 102, 103, 104) phases is well known, and the relation of quenching to the photoreaction of the quenched molecule, particularly in solution, has been the subject of several investigations (18, 20, 107).

The reversible nature of the quenching process in the adsorbed and dissolved phases indicates that a photoreaction is not the primary quenching process as suggested for aniline in the vapor phase (104). The simple process



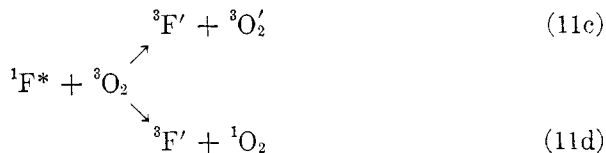
assumes that the electronic energy of F^* , which may be of the order of 100 kcal./mole, is transformed into vibrational energy of the colliding partners, and moreover is not specific for paramagnetic molecules.

Kautsky (39) has suggested that quenching by oxygen results in the electronic excitation of the oxygen molecule to one of its low-lying singlet states, $^1\Sigma$ at 37 kcal. or $^1\Delta$ at 22, 27, and 31 kcal. above the ground state (28). This process, which may be written



would explain the quenching inability of most inert gases which have no such low-lying electronic levels, but would be expected to have a low probability in the absence of spin conservation which is an important factor in simpler systems (43). Moreover it is found that the nitric oxide molecule, with a lowest excited state $^2\Sigma^+$ at some 126 kcal. above the ground state, is just as efficient a quenching molecule as oxygen (26, 33, 48, 90), and the interpretation of quenching as an energy-transfer process cannot be upheld in this case (33).

The theory of paramagnetic quenching introduced by Terenin (97) recognizes the lower-lying triplet state of the fluorescent molecule. According to this theory the restrictions attending singlet \rightarrow triplet transitions are removed by collision with the paramagnetic oxygen molecule with the possible results



Of these, Terenin considered process 11d the most probable, since the requirements of spin conservation are met. Moreover, process 11d reduces the amount of energy which must be taken up vibrationally between the colliding partners and requires that the energy liberated in the singlet \rightarrow triplet conversion should be sufficient to excite the oxygen molecule to its singlet state, i.e., F^* should lie at least 22 kcal. higher than 3F . From his suggested association of phosphorescence emission with 3F , Terenin assigned the range of energy values 35–70 kcal. to the latter and predicted that the fluorescent state must have an energy of at least 57 kcal., corresponding to absorption at 5000 Å., for quenching to take place by process 11d.

Karyakin (31) subsequently investigated twenty-five derivatives of anthraquinone in the vapor phase and found that of eleven which did not react with oxygen in the dark at 300°C., those with an absorption maximum in the range 4500–4800 Å. were reversibly quenched by oxygen, whilst those with maxima in the region 5500–5600 Å. were unaffected. However, further quenching studies carried out with the same derivatives in both adsorbed and vapor phases, using the paramagnetic nitric oxide molecule, produced parallel results (33); in view of the large energy required for the electronic excitation of nitric oxide this result eliminates 11d as the quenching process.

Despite the infringement of spin conservation requirements, process 11c appears to be the most tenable at the present time. It has been suggested that the fluorescent and triplet levels should lie within 5 kcal. of each other for quenching to occur (32), but in view of their large separation of 28.7 kcal. in anthracene and 15.5 kcal. in aniline (34), both of which are strongly quenched, this requirement does not appear to be essential. The energy liberated during the singlet \rightarrow triplet transition can be readily accommodated by the latter state (43) until it is dissipated by further collision, and the formation of photoproducts (20, 107) would then result from secondary processes involving the metastable biradical (18, 97).

The interpretation of quenching by paramagnetic molecules as a collision-induced singlet \rightarrow triplet transition provides a further example of the influence of strong external magnetic fields on spin intercombinations (35, 37).

2. Diamagnetic molecules

(a) *Carbon tetrachloride*: In view of the "heavy-atom" effect on spin-orbital coupling forces (35, 50) it is reasonable to suppose that this molecule quenches the

fluorescence of β -naphthylamine (22) by promoting a radiationless singlet \rightarrow triplet transition on collision. The quenching of the fluorescence of anthracene in solution has received interpretation along these lines (18), and the absence of fluorescence emission by chlorobenzene (6), discussed in relation to the spontaneous transition 3b, suggests that the field near the chlorine nucleus is sufficiently powerful to effect this transition (50). The low efficiency of collisional quenching (see table 3) compared with oxygen may signify that a closer penetration (36) of the colliding molecules is required than that afforded by a kinetic collision.

Carbon tetrachloride has no effect on the fluorescence intensity of anthracene vapor however (90), and its quenching of β -naphthylamine may be the result of a photoreaction involving the amino group. The constant rate of decrease in the fluorescence intensity of this vapor, following the initial sharp reduction when carbon tetrachloride is first added (22), certainly suggests a mechanism of this type. It is unfortunate that the reversibility of the quenching process in the vapor phase is difficult to demonstrate in the majority of cases.

(b) *Sulfur dioxide*: Using a static system, Bowen and Metcalf (16) found that sulfur dioxide quenched the fluorescence of anthracene vapor with the same efficiency as oxygen. This may be due to the heavy-atom effect of sulfur described above, although the high efficiency would not be expected. It was later found, however (90), that a marked reduction in the absorbing power of anthracene at 3660 Å. took place on the addition of this quenching molecule; the effect increased both with time and with concentration of the quencher, and the measured quenching constant under flow conditions was found to increase with pressure of sulfur dioxide. These results were interpreted in terms of a reaction of the sulfur dioxide with both ground and excited states of the fluorescent molecule, and a collisional quenching efficiency is obtained which is close to the value for carbon tetrachloride (see table 3). The high value of the quenching constant for sulfur dioxide recently obtained under flow conditions and its independence of flow rate (53) suggest that the above interpretation is insufficient; however, the absence of absorption data in the presence of sulfur dioxide makes it impossible to determine how much of this large quenching effect involves the excited fluorescent molecule.

TABLE 2
Dependence of quenching of fluorescence of anthracene vapor on temperature

Quenching Molecule	Concentration	K_Q		E_Q
		200°C.	300°C.	
		<i>l./mole</i>	<i>l./mole</i>	
	<i>moles/liter</i>			<i>cal.</i>
SO ₂	5×10^{-4}	2180 \pm 60	2210 \pm 14	630
O ₂	10^{-3}	932 \pm 3	917 \pm 4	590
HI.....	2×10^{-3}	291 \pm 10		
CH ₃ I.....	1.2×10^{-2}	77.4 \pm 2	59 \pm 0	1940
C ₂ H ₅ I.....	1.2×10^{-2}	104 \pm 3	79 \pm 3	1900
C ₃ H ₇ I.....	7×10^{-3}	182 \pm 10	139 \pm 2	1860
Aniline.....	9×10^{-3}	90 \pm 6	47	4000

TABLE 3
Lifetimes from quenching data

Fluor	Quencher	λ	T	K_Q	ρ	τ_F	τ_Q	$10^9\tau_0$	References
		\AA .	$^{\circ}\text{C}$.	<i>l./mole</i>		\AA .	\AA .	<i>sec.</i>	
Aniline.....	O ₂	2878	70		1	3.0	1.5	7.9	(55)
β -Naphthylamine.....	O ₂	3660	130		1	3.5	1.5	16.2	(56)
	CCl ₄	2650	120	950	0.4*	3.9	1.7	16.2	(22, 23)
	CCl ₄	3130	120	950	0.4*	3.9	1.7	16.2	(22, 23)
Anthracene.....	Self	3660	300	1280	1	3.3	3.3	4.2	(90)
	O ₂	3660	300	1000	1	3.3	1.7	3.2	(90)
	O ₂	3660	340	1070	1	3.3	1.7	3.4	(90)
	O ₂	3660	220		1	4.1	1.5	2.0	(83)
	NO	3660	280	1120	1	3.3	1.7	3.5	(90)
	HI	3660	200	290	0.4*	3.3	2.0	3.5	(53)
	SO ₂	3660	280	340	0.3*	3.3	2.5	3.5	(90)
9-Phenylanthracene.....	O ₂	3660	300	1260	1	4.3	1.7	2.8	(90)
	NO	3660	300	1380	1	4.3	1.7	3.0	(90)
9,10-Diphenylanthracene ..	Self	3660	300	2200	1	5.1	5.1	4.1	(90)
	O ₂	3660	300	1850	1	5.1	1.7	3.3	(90)
Anthraquinone.....	O ₂		300		1			1.3-9.1	(31)
Anthrone.....	O ₂		300		1			5.4	(31)
β -Aminoanthraquinone.....	O ₂		300		1			5.4	(31)
β -Methylanthraquinone.....	O ₂		300		1			2.3	(31)

* Calculated assuming τ_0 .

(c) *Cyanogen*: Neporent (55) observed a reduction in the fluorescence intensity of aniline vapor on the addition of cyanogen. As this author pointed out, cyanogen rapidly polymerizes or reacts with aniline under the influence of ultraviolet radiation, and the deposition of opaque products on the cell walls made quantitative measurements impossible.

(d) *Hydrogen iodide and alkyl iodides*: The quenching of the fluorescence of anthracene by these gases (53), shown in table 2, may be attributed to the collisionally induced spin intercombination promoted by the heavy iodine atom, which has been visually demonstrated in the liquid phase (36). The collisional quenching efficiency of hydrogen iodide is some 30 per cent of the value calculated for paramagnetic molecules (table 3) and is close to that for carbon tetrachloride obtained from β -naphthylamine quenching.

The long-wave end of the absorption continua of hydrogen iodide (28), methyl iodide (70), and ethyl iodide (69) is at 3600 \AA ., close to the wavelength used for excitation (3660 \AA .), and the possibility of inner-filter effects at the prevailing temperatures of 2 to 300°C. cannot be ruled out.

(e) *Self-quenching*: In this case neither the paramagnetic nor the heavy-atom quenching mechanism can be invoked. Although triplet-level formation has been observed in anthracene vapor in the absence of paramagnetic molecules or heavy atoms (72), it is unlikely that the triplet level is the self-quenching agent, since its photostationary concentration is too small to account for the magnitude of

the observed effect (90). Triplet-level formation may be the result of self-quenching in this case according to expression 12a.



For anthracene with excited singlet and triplet levels at 27,600 and 14,700 cm^{-1} , respectively, above the ground state (44, 68), process 12a would be energetically feasible, but as a result of their triplet-level absorption studies, Porter and Wright (72) conclude that triplet formation from the fluorescent state is essentially the first-order process 3b followed by collisional stabilization.

In those cases where self-quenching has been quantitatively studied, it is found to be as efficient as paramagnetic quenching (90), and the fluorescence of acetone, as distinct from its phosphorescence (38), is subject to self-quenching whilst oxygen has no effect (48).

(f) *Aniline*: A small quenching effect has been observed in anthracene vapor on the introduction of aniline (53, 83). In view of the weak excitation of aniline anti-Stokes fluorescence (73) under conditions similar to those employed, however, the interpretation of this quenching as an inner-filter effect should be considered.

C. THE INTERPRETATION OF QUENCHING DATA

If r_F and r_Q are the radii of fluorescent and quenching molecules and M_F and M_Q are their molecular weights, respectively, then the ratio of collisional deactivation to emission rate constants given by expression II becomes

$$K_Q = \frac{k_q}{k_f} = p\tau_0 \frac{N}{1000} (r_F + r_Q)^2 \left\{ 8\pi RT \left(\frac{1}{M_Q} + \frac{1}{M_F} \right) \right\}^{1/2} \exp(-E_Q/RT) \quad (\text{XIX})$$

where N is Avogadro's number, R is the gas constant, T is the temperature of the vapor, and E_Q is the activation energy of the quenching process.

The analysis of quenching data involves the assignment of values to two of the quantities p , τ_0 , and r and evaluation of the third on the assumption that E_Q is zero.

1. The activation energy of the quenching process

The estimation of E_Q from quenching measurements requires the determination of the temperature coefficients of all other photokinetic processes which are operative under the conditions of observation. Neporent (56) established that the quenching of β -naphthylamine fluorescence by oxygen is temperature-independent over the range 130–193°C. when the incident wavelength is such (3660 Å.) that no first-order dark deactivation takes place. The quenching by oxygen of the long-lived fluorescence of acetone is also temperature-independent between 32°C. and 75°C. (67), and the increased quenching of the fluorescence of anthracene by oxygen with temperature is only slightly greater than would be expected from the increased collision rate (16).

More recently Metcalf (53) has investigated the quenching effect of several gases on the fluorescence of anthracene excited by the 3660 Å. line at 200°C.

and 300°C. His results, given in table 2, show a negative temperature coefficient and are expressed as

$$K_Q = AT^{1/2} \exp(+E_Q/RT)$$

where A is the temperature-independent factor in expression XIX. Metcalf compared E_Q with E' , calculated from the temperature dependence of viscosity η , using the expression

$$\eta = \eta_0 T^{1/2} \exp(+E'/RT)$$

and concluded that the negative temperature coefficients of quenching are no greater than can be attributed to the attractive forces between the fluorescent and quenching molecules. The experimental values of E_Q are small however, and in the case of oxygen and sulfur dioxide the measured quenching constants at the two temperatures are almost identical within the remarkably small experimental error.

Some theoretical evidence may be adduced in support of the assumption that E_Q is zero. There is little doubt that transitions from higher vibrational levels of the fluorescent state take place during fluorescence emission (13, 57, 86), which is therefore represented by both processes 4 and 10. The complex expression VI reduces to VII only if the rate constants of processes 8 and 11, and 9 and 12, are the same; in the absence of processes 2 and 3 expression VII is that proposed by Stern and Volmer, which satisfactorily expresses the quenching data in almost all cases.

2. The lifetime of the fluorescent state

In the absence of internal or collisional perturbations the lifetime τ_0 of the excited molecule is equal to the reciprocal of the emission rate constant, i.e.,

$$\tau_0 = 1/k_{10}$$

The estimation of τ_0 from quenching data involves assumptions concerning the probability p of quenching on collision and the application of a correction for processes 2 and 3 where these occur. The following arguments have been presented for the assumption that, at least in the case of paramagnetic quenching, p is unity.

(a) If quenching by oxygen and nitric oxide is to be interpreted as a collision-induced radiationless singlet \rightarrow triplet transition under the influence of their magnetic fields, it would be expected that oxygen with an effective Bohr magneton number μ_{eff} of 2.83 would be more efficient than nitric oxide, for which μ_{eff} is 1.92 at 300°C. (101). That both gases are equally efficient in quenching the fluorescence of acetone (48), anthracene (90), anthraquinone derivatives (33), and β -naphthylamine (26) is a strong indication that quenching takes place at every collision (90).

(b) At low aniline pressures, the introduction of inert gases strongly increases the intensity of some lines in the resonance spectrum, in particular the line at 2957.6 Å. These gases have no effect on the absorption spectrum; therefore in-

tensification must be due to a collisional redistribution of vibrational energy of the excited molecule. Oxygen strongly quenches the resonance emission but has no effect on the relative intensities of the resonance lines; it is therefore concluded that every collision between an excited aniline molecule and oxygen leads to quenching (55, 102). This argument also supports the assumption that process 7 does not take place.

(c) Neporent (56) states that the satisfactory agreement between values for the fluorescence yield of β -naphthylamine measured directly and the values calculated from quenching by oxygen on the assumption that p is unity, indicates that this assumption is correct. However, since γ is calculated as the ratio τ/τ_0 , where τ is the lifetime in the presence of first-order deactivation processes 2 and 3, this agreement would still hold if p were not unity but had the same value in each determination, i.e., $\gamma = p\tau/p\tau_0$; as it has been shown that p is independent of the wavelength used for excitation (55), the validity of this argument is doubtful.

Values of τ_0 calculated from quenching data on the assumption that $p = 1$ and using radius values determined from transport phenomena or calculated from molecular models are given in table 3.

By definition the lifetime of the excited molecule is equal to the reciprocal of the sum of probabilities of first-order or second-order deactivating processes. Thus processes 2 and 3 reduce the unperturbed lifetime τ_0 to τ , where

$$\tau = 1/(k_2 + k_3 + k_{10}) \quad (\text{XX})$$

and equation XVII becomes

$$f_0/f = 1 + p\tau z \quad (\text{XXI})$$

On the justifiable (102) assumption that $p = 1$, Neporent used equation XXI to obtain the values of τ given in table 4 from his quenching data (56).

3. The collisional efficiency of the quenching process

If a reliable value for the lifetime of the excited molecule is available independently, quenching data may be used to determine the collisional quenching probability p . Several authors have preferred to express their results in this way.

Since the probability of emission is equal to the probability of the reverse transition, τ_0 is related to the area under the corresponding absorption band $\int \epsilon' d\bar{\nu}$ with a maximum at $\bar{\nu}_A$ by expression XXII (45)

$$1/\tau_0 = 8\pi cn^2 \bar{\nu}_A^2 \int \epsilon' d\bar{\nu} \quad (\text{XXII})$$

where ϵ' is the extinction coefficient in natural units, c is the velocity of light in a vacuum, and n is the refractive index of the medium. Bowen and Metcalf (16) used expression XXII to obtain $\tau_0 = 1.33 \times 10^{-8}$ sec. for the excited anthracene molecule from its absorption band in the near ultraviolet, and concluded from their data that oxygen and sulfur dioxide quench the excited anthracene molecule once in every two to six collisions.

TABLE 4

*Lifetimes ($\tau \times 10^{-8}$ sec.) of excited β -naphthylamine molecule from oxygen quenching (56)**

T	$\lambda = 3660 \text{ \AA.}$	3341 \AA.	3129 \AA.	3022 \AA.	2804 \AA.	2652 \AA.	2537 \AA.
$^{\circ}\text{C.}$							
130	1.62	1.51	1.30	1.19	0.815	0.385	0.195
151	1.62	1.41	1.24	1.12	0.685	0.355	0.165
172	1.62	1.33	1.12	1.04	0.600	0.265	0.140
193	1.62	1.28	1.08	1.00	0.465	0.230	0.105

* Calculated from equation XXI, using $\tau_F = 3.5 \text{ \AA.}$ and $\tau_O = 1.49 \text{ \AA.}$

The phase-shift technique has recently been employed to measure decay constants directly in both the dissolved and the crystalline states (4, 47); the high accuracy of this method is somewhat offset by reabsorption effects (4). Bowen has discussed the values obtained for anthracene in this way with those obtained less directly in solution, and uses the most consistent value to interpret vapor-phase quenching data on the reasonable assumption that τ_0 is the same in all phases; he concludes that for oxygen and nitric oxide p is approximately 0.3 (15).

Analysis of the quenching of the phosphorescence of biacetyl by oxygen leads to 0.0095 for p (38). This remarkably low value for the collisional quenching probability between two biradical states suggests that a primary photooxidation with stringent steric requirements is responsible.

4. The quenching radius

Stevens (88) has defined a quenching collision and uses values obtained for the lifetime in solution from expression XXII to obtain a self-consistent set of quenching radii. These are some 60 per cent of the gas kinetic values and are compared with the dimensions of the π -electron systems and paramagnetic fields of the fluorescent and quencher molecules, respectively.

V. QUANTITATIVE ASPECTS OF FLUORESCENCE STABILIZATION

A. FIRST-ORDER DEACTIVATION OF THE POTENTIALLY FLUORESCENT MOLECULE

If the fluorescence yield is unity at very low pressures in the absence of quenching gas, processes 2 and 3 may be assumed nonoperative as in the case of anthracene excited by the 3660 \AA. line at 300 $^{\circ}\text{C.}$ A lower yield in the absence of second-order perturbations may be due to either process 2 or process 3 or both as suggested for 9,10-diphenylanthracene (90); in this molecule the energy of the carbon-carbon bonds is close to the energy of the absorbed quantum (78 kcal. at 3660 \AA.), whilst in support of process 3 the suggested temperature-dependent internal dissociation to the biradical or triplet level (30) may be cited.

In the absence of data on fluorescence yield, the stabilization or enhancement of fluorescence by the introduction of inert gases may be taken as a definite indication that process 2 or 3 is taking place; an analysis of photoproducts, which would be different in each case, will establish whether the deactivation is due to dissociation or to a singlet \rightarrow triplet transition. The rate of both processes increases with the vibrational energy reserve of the excited molecule, and the resulting

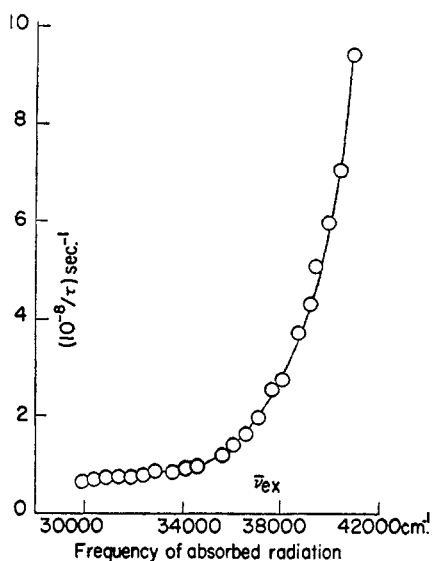


FIG. 12

FIG. 12. Dependence of lifetime τ of excited β -naphthylamine molecule on frequency $\bar{\nu}_{ex}$ of absorbed radiation (56).

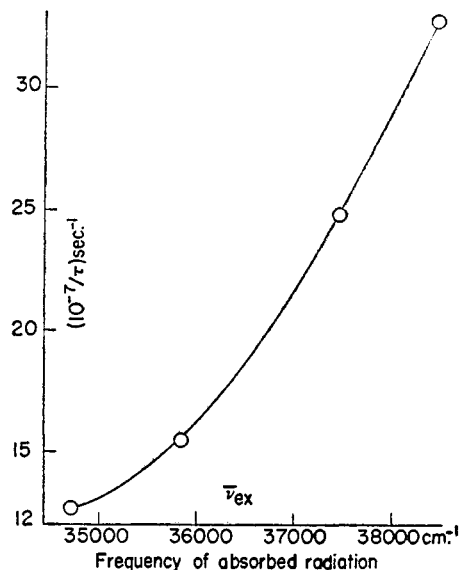


FIG. 13

FIG. 13. Variation of lifetime τ of excited aniline molecule with frequency $\bar{\nu}_{ex}$ of absorbed radiation (56).

variations of both lifetime and fluorescence yield with the magnitude of the absorbed quantum are shown in figures 5, 12, and 13.

The lifetime of the β -naphthylamine molecule calculated from quenching by oxygen under various conditions is given in table 4. At 3660 Å. processes 2 and 3 do not take place and $\tau = \tau_0 = 1/k_{10}$; whence $k_2 + k_3$ may be calculated for the rest of the data in table 4 from expression XX.

The probability $d = k_2 + k_3$ of dark deactivation is found to increase exponentially with the reserve of vibrational energy E of the excited molecule, and Neporent (56) proposed the empirical relationship

$$d = A \exp[\alpha(\bar{\nu}_e + q)] \quad (\text{XXIII})$$

involving constants A and α , the frequency $\bar{\nu}_e$ of the absorbed radiation, and the measure q of the thermal contribution to E , equivalent to 24 cm.⁻¹/°C. in this case. The appropriate plot is shown in figure 14, and the divergence of the low-energy data is attributed (56) to the nonequivalence of the optical and thermal excitation of vibrational energy when this is small; the simultaneous operation of processes 2 and 3 could conceivably produce the same effect.

Boudart and Dubois (13) have assigned a vibrational temperature T_{vib} to the molecule excited by the frequency $\bar{\nu}_e$ at temperature T , defined by

$$T_{vib} = T + (\bar{\nu}_e - \bar{\nu}_0)/C_{vib} \quad (\text{XXIV})$$

where $\bar{\nu}_0$ is the O'-O'' transition frequency and C_{vib} is the vibrational heat capa-

city of $24 \text{ cm.}^{-1}/^{\circ}\text{C}$. From a suitable plot of the higher-energy data, the first-order rate expression is found to be

$$d = 0.254 \times 10^{13} \exp[-(14,300/RT_{\text{vib}})] \quad (\text{XXV})$$

but the deviation of the lower-energy data is again apparent (92) and is attributed by these authors to the incomplete internal redistribution of the small amount of vibrational energy during the lifetime of the excited molecule. If this redistribution is incomplete it is difficult to understand why the fluorescence spectrum remains unchanged as E increases (56).

It is apparent that the spectral region investigated by Neporent covers two electronic band systems, and a treatment of the low-energy data obtained, following absorption in the first of these, leads to a value of $40 \text{ cm.}^{-1}/^{\circ}\text{C}$. for C_{vib} (92). The use of this value to obtain T_{vib}^* from expression XXIV leads to the expression

$$d' = 0.75 \times 10^{10} \exp[-(5600/RT_{\text{vib}}^*)] \quad (\text{XXVa})$$

for the low-energy data, which, it is suggested, refer to the radiationless spin-intercombination process 3b. Since T_{vib}^* ranges from approximately 400 to 600°C ., d' has the values 10^7 – 10^8 sec.^{-1} , which are well within the limits 10^6 – 10^9 sec.^{-1} suggested for this process (72).

Although the nature of these processes is uncertain in the case of β -naphthylamine, it has been established (55) that the first-order process competing with the

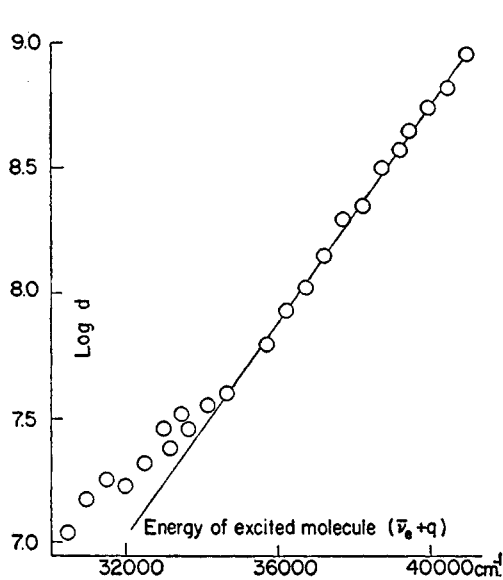


FIG. 14

FIG. 14. Variation of probability d of radiationless deactivation with energy of excited β -naphthylamine molecule according to expression XXIII (56).

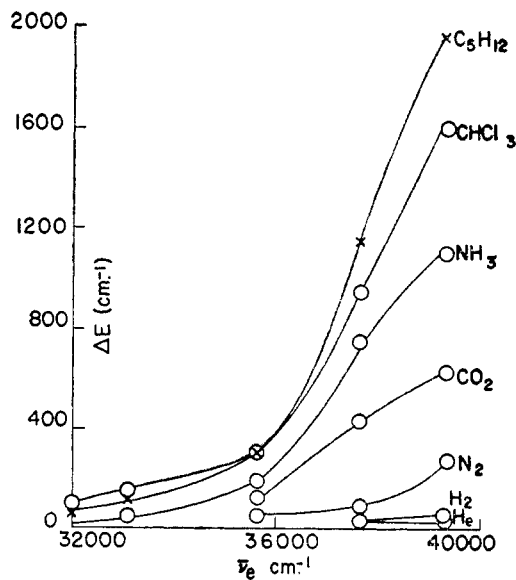


FIG. 15

FIG. 15. Variation of energy transferred per collision with total energy of β -naphthylamine molecule (57).

fluorescence emission of aniline involves rupture of the carbon-nitrogen bond. A similar treatment of the data for this molecule provides the expression (93)

$$d = 3.6 \times 10^{13} \exp[-(12,000/RT_{\text{vib}})] \quad (\text{XXVb})$$

and the similarity between this and expression XXV is certainly circumstantial evidence for the dissociation of β -naphthylamine at higher vibrational temperatures.

B. THE COLLISIONAL TRANSFER OF VIBRATIONAL ENERGY

The collisional stabilization of an energy-rich fluorescent molecule (processes 5, 6, and 7) leads to an increase in the overall fluorescence yield according to expression VII. Measurement of this increase as the pressure of stabilizing gas is increased enables the average amount of energy transferred per collision to be determined. This has been done in two ways.

1. Variation of the measured quenching constant with inert gas pressure

The quenching of β -naphthylamine fluorescence by carbon tetrachloride in the presence of the inert gases ethane and cyclohexane (22) has been discussed above (Section IV,A). The variation of the measured quenching constant with inert gas pressure is given by expression XV and shown in figures 3 and 4 of reference 22. Curme and Rollefson calculated k_7 from quenching data in the absence of inert gas, assumed that process 6 takes place at every collision, and, with Neporent's value for k_2 under the prevailing conditions, found the value of k_5 which, used in expression XV, gives the experimental curves at each exciting wavelength.

If the vibrational energy of the excited molecule is $(\bar{\nu}_e - \bar{\nu}_0)$ and its collision frequency with the inert gas is k_z , then the average amount of energy ΔE removed per stabilizing collision is given by

$$\Delta E = k_5(\bar{\nu}_e - \bar{\nu}_0)/k_z$$

The results obtained, shown in table 5, are of little quantitative significance in view of the fact that process 6 is assumed to take place at every collision; the interval between collisions under the prevailing conditions is approximately 10^{-7} sec., and this is so much greater than the reduced lifetime (10^{-8} - 10^{-9} sec.) of the excited molecule that it is unlikely that process 6 occurs at all.

TABLE 5

Average amount (ΔE) of vibrational energy transferred from β -naphthylamine molecule per collision (22)

$\lambda = 3130 \text{ \AA.}; T = 120^\circ\text{C.}$

Stabilizing Molecule.....	β -Naphthylamine	Carbon Tetrachloride	Cyclohexane	Ethane
$\Delta E \text{ cm.}^{-1}$	4000	250	250	100

2. Variation of fluorescence yield with inert gas pressure

This more elegant and direct method was first employed in the case of aniline (55, 100). At very low pressures in the absence of quenching gas expression VII becomes

$$\frac{1}{\gamma_x} = 1 + \frac{k_2 + k_3}{k_5[X] + k_{10}} \quad (\text{XXVI})$$

Thus if f_0 and f_x are the respective fluorescence intensities in the absence of inert gas and in its presence at concentration $[X]$, the relative intensification of fluorescence Δf is given by

$$\frac{1}{\Delta f} = \frac{f_0}{f_x - f_0} = \frac{\gamma_0}{\gamma_x - \gamma_0} = \frac{k_{10}}{k_2 + k_3} + \frac{k_{10}(k_2 + k_3 + k_{10})}{k_5[X](k_2 + k_3)} \quad (\text{XXVII})$$

The plot of $1/\Delta f$ against $1/[X]$ is linear and the slope/intercept ratio gives $(k_2 + k_3 + k_{10})/k_5 = 1/\tau k_5$. Since τ is known from quenching data on oxygen, k_5 may be calculated; the stabilizing efficiencies k_5/k_z obtained in this way are given in table 6.

This treatment has been refined more recently in its application to β -naphthylamine (13, 57). In the first place a correction is applied for the effect of inert gases on the absorption coefficient discussed in Section III,A above by using the ratio S of the stabilization $(f_x/f_0)_\lambda$, measured at the wavelength λ , to $(f_x/f_0)_{3660}$ measured at 3660 Å., where processes 2 and 3 do not take place and the change in fluorescence intensity is entirely due to the "partial weakening" effect (57, 58).

Secondly, it is recognized that the total vibrational energy E of the excited molecule is not removed by one particularly fortunate collision, but that successive collisions each remove a fraction of this energy to produce a descending series of vibrational levels with different probabilities of deactivation.

Neporent (57) treated this problem in a remarkably simple manner by noting the increase in fluorescence intensity produced at the frequency $\bar{\nu}$ when the pressure of added inert gas is such that each excited fluor molecule undergoes on the average one collision. The energy ΔE transferred by this collision is then equal to the reduction in frequency $\Delta \bar{\nu}$ required to produce the same intensification in the absence of inert gas. The results obtained are given in table 7.

Boudart and Dubois (13) have treated the multistage deactivation process

TABLE 6

Stabilization efficiency of inert gas molecules from enhancement of fluorescence of aniline vapor (55, 100)

λ	Ammonia	Ethylene	Nitrogen	Carbon Monoxide	Hydrogen
Å.					
2670	0.09	0.04	—	0.05	0.04
2598	0.09	0.05	0.06	0.07	0.08
2529	0.15	0.10	0.15	0.14	0.20

TABLE 7
Energy-transfer data from stabilization of fluorescence of β -naphthylamine

Gas	λ_{ex}	T	E	ΔE^*	ΔE^\dagger	α
	\AA	$^{\circ}\text{C}$	cm^{-1}	cm^{-1}	cm^{-1}	
CO ₂	2652	150	8460	550	430	0.5
	2537	150	10200	600	630	0.3
NH ₃	2652	150	8460	950	750	0.9
	2537	150	10200	1070	1100	0.8
	2652	190	8460	880	630	0.8
	2537	190	10200	1000	1250	0.7
C ₂ H ₁₂	2652	150	8460	1280	1150	0.2
	2537	150	10200	1690	1950	0.2
CHCl ₃	2652	190	8460	1240	1350	0.2
	2652	150	8460	1000	950	0.5
H ₂	2537	150	10200	1240	1600	0.5
	2652	150	8460	70	30	0.1
He.....	2537	150	10200	70	50	0.1
	2652	150	8460	70	30	0.2
N ₂	2652	150	8460	190	90	0.3
D ₂ †.....	2652	186	8460	60	—	
SF ₆ †.....	2652	186	8460	570	—	

* Neporent (57).

† Boudart and Dubois' treatment of Neporent's data (13).

‡ Boudart and Dubois' experimental data.

mathematically and show that if, as a result of its first collision, the lifetime of the excited molecule is increased from τ_1 to τ_2 , then

$$\left(\frac{dS}{dZ}\right)_{z=0} = \tau_2 - \tau_1 \quad (\text{XXVIII})$$

where Z is the collision frequency at inert gas concentration $[X]$, and $(dS/dZ)_{z=0}$ is the slope of the tangent to the stabilization curve (shown in figure 8) at zero $[X]$. As a result of this collision, an amount ΔE of vibrational energy is transferred, and the temperature of the inert gas molecule rises from T_1 to T_2 whilst that of the β -naphthylamine molecule falls from $T_{1\text{vib}}$ to $T_{2\text{vib}}$; thus if C is the heat capacity of X at constant volume

$$\Delta E = C_{\text{vib}}(T_{1\text{vib}} - T_{2\text{vib}}) = C(T_2 - T_1) \quad (\text{XXIX})$$

$T_{1\text{vib}}$ (and hence τ_1) is known from expression XXIV, and τ_2 (and hence $T_{2\text{vib}}$) is calculated from expression XXVIII; thus ΔE can be derived from expression XXIX. The results given in table 7 are also expressed in terms of an accommodation coefficient α , which is a measure of the approximation to equilibrium distribution of vibrational energy between the colliding partners and is defined by

$$\alpha = \frac{T_2 - T_1}{T_{2\text{vib}} - T_1} = \frac{C_{\text{vib}}}{C} \left(\frac{\Delta E}{E - \Delta E} \right)$$

This classical treatment of the vibrational energy of a complex molecule depends on the excitation of a large number of natural vibrations of different energies during intramolecular redistribution of initially excited mode, which together with the closely spaced rotational levels makes the collisional transfer of

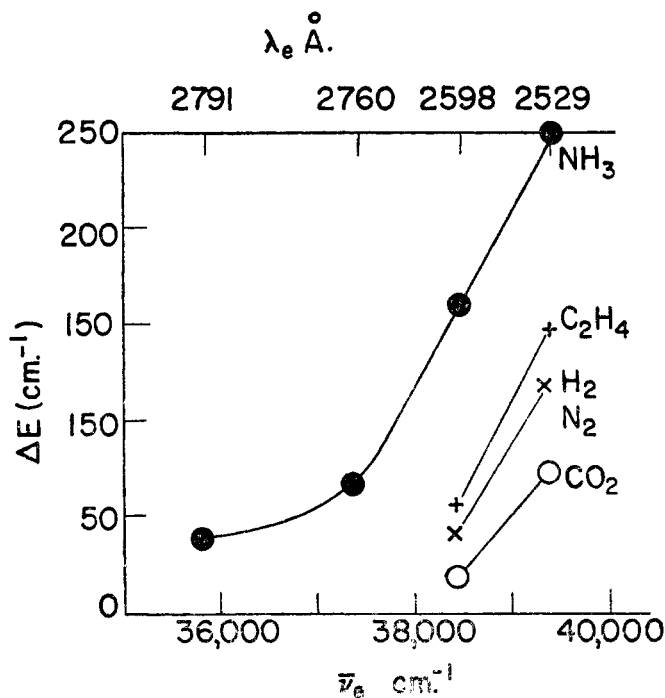


FIG. 16. Variation of energy transferred per collision with total energy of aniline molecule (57).

almost any quantity of energy possible and virtually removes the quantum restrictions (57). This is contrary to the behavior of simple molecules, where the transfer of quanta of larger energy is subject to strict requirements concerning the vibrational levels of the colliding molecules; the characteristics of the transfer process in these two extreme cases have recently been discussed (94).

It is interesting to note that although *n*-pentane removes some twenty times the energy taken up by the helium atom per collision, the efficiencies of these stabilizing gases expressed by α are the same. There is probably some correlation between the high accommodation coefficient of ammonia and the presence of an amino group in the fluorescent molecule, especially since rupture of the carbon-nitrogen bond would require a concentration of energy at this point; in support of this specificity, the pronounced effect of ethylene in stabilizing the benzene molecule (55) may be cited.

The increase in ΔE with the total vibrational energy reserve E is demonstrated for β -naphthylamine in figure 15 and for aniline in figure 16, which is obtained from earlier results (55) following the treatment outlined above (57). The point of inflexion corresponds to the value of E necessary for the internal redistribution of vibrational energy to be complete within the interval (57); it has also been attributed to the onset of a second unimolecular deactivation of higher activation energy which is therefore more susceptible to collisional suppression (92).

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A number of the other Russian papers are available as Technical Translations of the National Research Council of Canada. The author would like to thank the Translations Section of the N. R. C. Library in Ottawa for its cooperation in translating these papers.

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Note added in proof

Bowen and Veljković [*Proc. Roy. Soc. (London)* **A236**, 1 (1956)] have recently measured the stabilization of the fluorescence of perylene vapor by nitrogen, *p*-cymene, naphthalene, and hexamethylbenzene and find that, with the exception of naphthalene, the stabilization efficiency is proportional to the

molecular weight of the stabilizing molecule. The high efficiency of naphthalene is attributed to a longer collisional duration due to the interaction of π -bond orbitals which promotes thermal equilibration during the collisional process; this view is compatible with the observation that the average amount of energy transferred from the excited β -naphthylamine molecule on collision decreases as the temperature increases (table 7) despite the fact that more thermal energy is available at higher temperatures.

The absence of decomposition products indicates that in the case of perylene the collisionally suppressed deactivation process is the singlet \rightarrow triplet conversion (process 3b), for which a finite energy of activation must be necessary.