Excitation and Deexcitation of Benzene

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CONTENTS

I. INTRODUCTION

A large amount of spectroscopic data are now available for
benzene, providing much information on photophysics and photo-
chemistry properties of the lowest excited states of this molecule.
Nevertheless the nature of the various radiative and nonradiative
transitions involved in the deexcitation of the first excited
states is far from being completely understood.

This work reviews the photophysics and relevant photochemistry
of benzene in gas, liquid, and solid phases, with special em-
phasis on the experimental advances obtained by spectroscopic
techniques in the past few years. Throughout, the symbolism used
is that shown in the following reaction scheme:
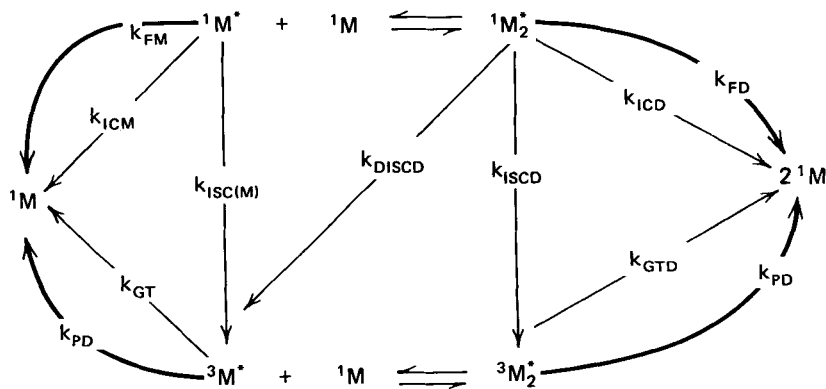
II. THE NATURE OF THE LOWER EXCITED STATES OF BENZENE

The near-ultraviolet spectral characteristics, and photo-
physical decay processes of benzene are generally described in
terms of transitions between the various π molecular orbitals
formed by linear combination of the carbon 2p atomic orbitals
which have symmetries b_{2g}, e_{2g}(two), e_{1g}(two), and a_{2u} within the

D_{6h} point group. Though the absolute energies and energy spacings of the orbitals are not known precisely, and are, to a degree, dependent upon the complexity of the calculatory method, the symmetries and ordering of energies generated by the simpler theories remain valid.

The ground state benzene configuration is $(a_{2u})^2$, $(e_{1g})^4$. Singly excited configurations are produced by promotion of an electron from one of the two degenerate e_{1g} orbitals to one of the degenerate e_{2u} orbitals (1). The predicted degeneracy of the states so produced (B_{2u}, B_{1u}, E_{1u}) is removed by electron interaction. Calculations (2) have shown that the ordering by energy of the transitions in which spin conservation is observed should be $^1E_{1u} > {}^1B_{1u} > {}^1B_{2u}$.

Experimental observations in the gas phase (3), solution (4), low-temperature glasses (5), rare gas matrices (6), and the crystal phase (7) have all confirmed that the lowest excited singlet state has symmetry, B_{2u}, and that a transition from the ground to this state occurs around 260 nm. Band intensity is very low (ε at λ (max) $\sim$ 250 (8))* as befits a symmetry forbidden, but vibrationally induced transition. Two more intense bands are observed on the high energy side of this $^1B_{2u} \leftarrow A_{1g}$ absorption; a medium-intensity band ($\varepsilon \sim 9000$ (8)) around 205 nm and a high-intensity band ($\varepsilon \sim 70,000$ (8)) around 190 nm.

The 205 nm band is widely believed to be the $^1B_{1u} \leftarrow {}^1A_{1g}$ transition though some controversy is still attached to this assignment. Several recent semi-empirical (9-11), and <u>ab initio</u> (11) calculations place an E_{2g} state, arising from a doubly excited π-π^{**} transition below the B_{1u} state arising from a single π-π^* excitation; supporting an early assignment (13) of the 205 nm band to a $^1E_{2g} \leftarrow {}^1A_{1g}$ transition. A doubly excited configuration may be of comparable energy to a singly excited configuration due to the sensitivity of the energy of the E_{2g} configuration to electron interaction. Contrary evidence comes from another <u>ab initio</u> calculation (14) which places the $^1E_{2g}$ state between the $^1E_{1u}$ and $^1B_{1u}$ π-π^* states. Still other calculations, semi-empirical (15) and <u>ab initio</u> (16) have placed the elusive $^1E_{2g}$ state above $^1E_{1u}$. It is clear from this confusing situation that even the most sophisticated computations presently available, incorporating multiple excited configurations and multicenter corrections, are unsatisfactory in assigning even relative energies to the doubly excited π-π^{**} states. This is apparently due to the extreme sensitivity of E_{2g} state energies to the values chosen for the resonance integrals (17).

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*Extinction coefficient units are M^{-1} cm^{-1} throughout the article.

The common assignment of the 205 nm band to the $^1B_{1u} \leftarrow {}^1A_{1g}$ transition is consistent with the expected ordering of state energies for those configurations arising from $e_{2u} \leftarrow e_{1g}$ excitation, and with the assigned position of $^1B_{2u}$. Despite early inconclusive reports (18), recent evidence from vibrational analyses of low temperature absorption data in rare gas matrices and films (19) and of reflection spectra (20) confirms the $^1B_{1u}$ assignment. However, electron impact spectra (21) under high resolution suggests that two electronic transitions occur in the 205 nm region; and this has been confirmed recently by absorption studies on benzene in perfluoro-n-hexane (22) and rare gas matrices (22,23), at low temperature. In these environments the shift in the $^1E_{2g} \leftarrow {}^1A_{1g}$ transition is greater than that of the $^1B_{1u} \leftarrow {}^1A_{1g}$ transition due to differences in the charge distribution of the configurations and allows separate observation of the two bands. Available experimental evidence favors the energy sequence deduced by Koutecky et al. (9):

$$^1E_{2g}^+ > {}^1E_{1u}^+ > {}^1B_{1u}^+ > {}^1E_{2g}^- > {}^1B_{2u}^- > {}^1A_{1g}$$

The high-intensity band ($\varepsilon \sim 70,000$) around 190 nm is usually assigned to the $^1E_{1u} \leftarrow {}^1A_{1g}$ symmetry-allowed π-π^* transition, though some contribution to the intensity may come from the superposition of the first member of one of the Rydberg series. The π-π^* assignment has been confirmed (24) from a vibrational analysis of the low-temperature spectrum of benzene in a rare gas matrix. Recent studies using multiphoton ionization spectroscopy have been considered to provide some indications of a $^1E_{1g}$ state as an alternative to assignments for the elusive $^1E_{2g}$ state (25). This conclusion awaits confirmation or otherwise by further experiments.

The relevant energies associated with each state are, to varying extents affected by the molecular environment, as discussed later. Table 1 contains approximate Franck-Condon maxima for the transitions from the $^1A_{1g}$ state.

In addition to transitions in the π manifold discussed above, some attention has been given recently to possible σ-π^* states in the ultraviolet nonradiative transitions from the $^1B_{2u}$ state. Callomon et al. (27) have postulated the transitions from higher vibrational levels of $^1B_{2u}$ to a $^3E_{2u}(\sigma$-$\pi^*)$ state to explain the onset of diffuseness in the high resolution absorption spectrum of vapor phase benzene in the 5.0 eV region. Ab initio (12,28) calculations have predicted the presence of at least one σ state (e_{2g}) lying between two filled π-molecular orbitals. Photoionization (29,30) experiments, and other evidence (31) appear to agree with the conclusion that a σ-π^* transition may be

TABLE 1. Approximate Franck-Condon maxima for transitions from $^1A_{1g}$ ground state to the lower lying π-electronic states

$^1E_{2g}^+$	$^1A_{1g}$	~ 7.25 eV[a]
$^1E_{1u}^+$	$^1A_{1g}$	~ 6.75 eV
$^1B_{1u}^+$	$^1A_{1g}$	~ 6.08 eV
$^1E_{2g}^-$	$^1A_{1g}$	~ 5.9 eV
$^1B_{2u}$	$^1A_{1g}$	~ 4.88 eV

[a]The location of the second E_{2g} state, $^1E_{2g}^+$ has been suggested by Birks (26), from an analysis of published data on $S_x \leftarrow {}^1B_{1u}$ absorption experiments.

expected in the ultraviolet region conventionally associated with π-π^* transitions. A recent CNDO -CI plus SO calculation by Minaev (32) has predicted a $^1A_{2u}(\sigma$-$\pi^*) \leftarrow {}^1A_{1g}$ transition at 5.11 or 5.98 eV depending upon the parameters chosen. Much of the earlier work, theoretical and practical, in the neglected consideration of σ-electron excitation has been reviewed by Burnelle and Kranepool (33). While most of the photophysical decay parameters of benzene that we shall discuss may be explained in terms of the lowest π-π^* singlet and triplet states, the mechanism of radiationless $S_1 \rightarrow S_0$ decay may involve the elusive $^1E_{2g}$ and σ-π^* states discussed above and their participation cannot be disregarded.

Since electron spin may invert during excitation, π-π^* triplet states, of the same symmetries as the previously described excited singlet states should exist. Again, electron interaction removes the degeneracy of these states, though the precise ordering of state energies is still a matter of some dispute. The ranking now generally accepted (34) is:

$$^3B_{2u} > {}^3E_{1u} > {}^3B_{1u}$$

a sequence for which there is considerable experimental and theoretical justification (35).

There is no interference in the lower π-π^* manifold from the $^3E_{2g}$ states; both recent calculatory (12,16,17,36) and experimental (37) evidence place the lowest energy $^3E_{2g}$ configuration above the $^3B_{2u}$ state. Again, the relevant energies of the various states are dependent, to a degree, on the molecular environment, and in this case are more difficult to determine experimentally because of the multiplicity as well as symmetry forbidden nature of transitions from the ground state.

The selective data on Franck-Condon maxima for transitions from $^1A_{1g}$, recorded in Table 2, were obtained from electron impact (38) and $T_x \leftarrow {}^3B_{1u}$ transient absorption studies (39). They are considered at this stage to illustrate the relative positions of the triplet states vis-à-vis the singlet states discussed earlier.

TABLE 2.   Approximate Franck-Condon maxima for transitions from $^1A_{1g}$ ground state to the lower lying triplet π-electronic excited states.[a]

$^3E_{2g}$	$^1A_{1g}$	$\sim$ 6.55 eV
$^3B_{2u}$	$^1A_{1g}$	$\sim$ 5.60 eV
$^3E_{1u}$	$^1A_{1g}$	$\sim$ 4.75 eV
$^3B_{1u}$	$^1A_{1g}$	$\sim$ 3.95 eV

[a]Data from refs. 38 and 39.

No information is available concerning σ-π^* transitions, though from the approximate singlet assignments and presuming validity of Hund's Rule a σ-π^* state or states may be expected to be within the energies of the lower π-π^* manifold. It is interesting to speculate that the radiationless $T_1 \rightarrow S_0$ decay, explained with such difficulty in theoretical analyses of the benzene problem, may involve a transition to a previously unconsidered $^3(\sigma$-$\pi^*)$ state.

III. TRANSITION BETWEEN THE LOWER ENERGY STATES

Interstate transitions are generally considered to be governed principally by the familiar symmetry and multiplicity

selection rules. The manner in which these rules affect the major excitation and decay routes of benzene are discussed below.

A. Excitation from the $^1A_{1g}$ State

Within the singlet manifold of the lower energy transitions only the $^1E_{1u} \leftarrow {}^1A_{1g}$ excitation is symmetry allowed, though transition to any of the $^1B_{1u}$, $^1E_{2g}$, and $^1B_{2u}$ states can be promoted by coupling of the "pure" electronic states with vibrations of symmetry (b_{2g}, e_{2g}), (e_{2u}, b_{1u}, b_{2u}, e_{1u}), and (e_{2g}, b_{1g}), respectively. As mentioned above, all four transitions may be observed under certain circumstances, although $^1E_{1u} \leftarrow {}^1A_{1g}$ is, as expected, the most intense. The selection rules for double photon excitation predict that the modes of b_{1u}, b_{2u}, e_{2u} and e_{1u} symmetry should induce the absorption (40). Studies carried out by Hochstrasser, Sung, and Wessel (41) on a single crystal of benzene at 2^oK show that a certain number of vibrations of b_{1u}, b_{2u}, e_{1u}, and e_{2u} symmetry can be assigned in the two photon absorption spectrum. Gas phase two photon absorption spectra for benzene were reported recently by Wunsch, Neusser, and Schlag (42), who have found that the most powerful mode is of b_{2u} symmetry which is the extremely weak the ν_{19} mode of e_{1u} symmetry. Definitive experiments on the excited states of benzene using this promising technique are awaited.

For excitation into the triplet manifold, the transition $^3E_{1u} \leftarrow {}^1A_{1g}$ has first-order spin-orbit allowedness, while the $^3B_{1u} \leftarrow {}^1A_{1g}$ transition requires vibronic coupling via e_{2g}, b_{1g}, or D_{2g} modes or combination tones. Absorption studies (39) on oxygen free crystalline benzene have revealed a weak $T_2 \leftarrow S_0$ transition, but no $T_1 \leftarrow S_0$ transition, confirming the relative allowedness of the two transitions. Furthermore, an enhancement of the $T_1 \leftarrow S_0$ absorption induced by high pressures of oxygen was recently reported for benzene and for a large number of simple benzene derivatives (43).

No experimental evidence is available for the $^3B_{2u} \leftarrow {}^1A_{1g}$ transition which is both spin and symmetry forbidden in the first order, and should occur in the same spectral region as the medium-intensity $^1B_{1u} \leftarrow {}^1A_{1g}$ transition.

B. Emission to the $^1A_{1g}$ State

Kasha's Rule (44) requires that emission should occur from the lowest $^1B_{2u}$ and $^3B_{1u}$ states in benzene. This is essentially the case though a predictable very weak emission has been reported recently from higher states of oxygen-quenched benzene in gaseous (45) and solution (46) phases. The major fluorescence

and phosphorescence processes for benzene are thus forbidden, and the radiative decay probabilities may be influenced by the environment as will be discussed below.

C. Transitions Between Excited Singlet and Triplet States

Intersystem crossing from the $^1B_{2u}$ envelope of vibronic states is thought to occur from the lowest vibrational level, or perhaps the lowest two or three such levels. Given the lower relative energies of $^3E_{1u}$ and $^3B_{1u}$ states, transitions to each of these configurations from $^1B_{2u}$, are possible. There is first-order spin-orbit allowedness in that to the $^3B_{1u}$ state, but vibronic coupling is required for the transition to $^3E_{1u}$. Experimental evidence for intersystem crossing from higher electronic states is lacking, but there is no reason to neglect this route in the consideration of the decay processes of benzene molecules that have been so excited.

IV. EXCITED STATE GEOMETRY

The ground state of the benzene molecule is perfectly hexagonal and the molecular wave functions may be used as bases for irreducible representations of the D_{6h} point group. Transitions between the molecular energy states are usually excited in terms of the symmetry restrictions of this point group. The forbidden nature of the lower energy electronic transition has led to considerable discussion about the geometry of the excited states involved, since even slight deviations from regularity lead to reduction in symmetry, and require consequent modification of the selection rules. Despite early indications (47) that the phosphorescence spectrum may be explained using regular hexagonal symmetry, and recent evidence (48) the D_{6h} symmetry is maintained for $^3B_{1u}$ benzene in cyclohexane at 77°K, there is much evidence to show that the molecule is distorted when in the $^3B_{1u}$ state. Thirty years ago, Lewis and Kasha (49) presented evidence for a molecular contraction along the 1-4 axis, from analysis of phosphorescence data. Further results from gas phase $^3B_{1u} \leftarrow ^1A_{1g}$ oxygen-perturbed absorption spectra (50) led to a D_{2h} assignment of the upper state. van der Waals and co-workers (51-55) have shown by ESR studies that the vibronic coupling in the triplet manifold between $^3B_{1u}$ and $^3E_{1u}$ via the e_{2g} vibrational mode plays the dominant role for the phosphorescence process and that this leads to a non hexagonal phosphorescent state distorted to a quinoidal form. Gwait et al. (56), using phosphorescence microwave double resonance, have studied the zero field origin of the

0,0 band of phosphorescence of benzene-h_6 in benzene-d_6 at $1.6^{\circ}K$. The results obtained are consistent with a $^3B_{1u}$ assignment for a distorted D_{2h} benzene phosphorescent state and the lowest triplet of toluene is also shown to have an expanded quinoidally distorted ring by the calculations of Haaland and Nieman [57]. Evidence for a D_{2h} assignment of the lowest triplet state in solid phase was also provided by other authors [58,59].

Due to the highly forbidden nature of the $^3B_{1u} \leftarrow {}^1A_{1g}$ absorption, observations are only possible in perturbed systems such as in the presence of oxygen or in solid matrices, and it has been suggested that the symmetry distortions that have been deduced may arise from the influence of the molecular environment, rather than a genuine geometric property of the isolated molecule. While this possibility cannot be overlooked, theoretical considerations support the view that the $^3B_{1u}$ state is inherently distorted. Davaquet [60] has shown that the vibrations that stabilize the free $^3B_{1u}$ molecules are precisely those that would cause a slight distortion similar to that suggested for the solid phase triplet molecule. Fujimura, Yanaguchi, and Nakajima [61] have calculated the $^3B_{1u}$ state to have quinoidal D_{2h} symmetry in agreement with an earlier theoretical analysis [62]. These authors predict that the $^1B_{1u}$ state will also be distorted with antiquinoidal D_{2h} symmetry, and maintain that the lowest excited singlet state $^1B_{2u}$ will retain D_{6h} symmetry, albeit with a slightly enlarged ring. This is not in agreement with conclusions of Nieman and Tinti [58] who have interpreted experimental results on the absorption, fluorescence, and phosphorescence of several isotopic benzenes in terms of a distortion of both the $^1B_{2u}$ and $^3B_{1u}$ states.

It is worthy of note that the photochemical production of Dewar benzene from the $^1B_{1u}$ state [63] and from the $^3B_{1u}$ [64,65] is consistent with the quinoidal deformations suggested for these states.

A distortion of the $^1B_{2u}$ state of benzene to D_{3d} has also been proposed [66] to account for inconsistencies in the interpretation of the ultraviolet spectrum of pure crystalline benzene at low temperatures. Such distortions may be the result of the solid medium or, more probably, the spectral inconsistencies may be due to state splitting by the environment.

V. THE INFLUENCE OF THE ENVIRONMENT ON THE ELECTRONIC STATES

The influence of different environments on molecular states has been studied, theoretically and practically, from changes in the absorption spectra. Such effects as frequency shifts, peak width changes, and variation of oscillator strength for various

transitions are measures of the relative effects of different environments on the state involved.

The first absorption band of benzene shifts slightly to the red ($\sim$ 200 – 300 cm^{-1}) with the change between vapor phase and solution, and further shifts dependent upon the nature of the solvent occur. The extent of such red shifts may be related qualitatively to medium refractive index and dielectric constant. Several theoretical approaches to the problems of spectral shifts have been attempted (67), but in general these are more useful for polar molecules, and to allowed transitions where shifts are of greater magnitude. Suffice to say that in benzene there is no discontinuity in the trend of shifts with refractive index, through gas, liquid, and solid phases, other than indicating that the forces of interaction between this molecule and the environment are weak. The crystalline phase is exceptional, since the "strict" selection rules for transition are broken down by interaction with the crystal field, which leads to factor group splitting (68) and the appearance of four (69) components of the 0-0 band, all of which are shifted.

Much experimental evidence is available on the small solvent shifts which are measureable but, since little effect on the photophysical decay processes is expected, no review of this work will be attempted; the reader is referred to the work of Eastman and Rehfeld (70) who report data for benzene in the vapor phase and in 37 different solvents.

Changes in oscillator strength are expected since this is a function of the refractive index of the medium (71), though the effect is much smaller than theoretically expected in the case of benzene. To a first approximation the oscillator strength for the $^1B_{2u} \leftarrow ^1A_{1g}$ transition is independent of molecular environment (70).

A typical environmental effect on $S_1 \leftrightarrow S_0$ transitions concerns the vibrational structure of the spectra. Loss of structure in solution relative to vapor and solid phases is the result of specific solute-solvent interactions and as such, is dependent upon the dielectric properties of the solvent. Lawson, Hirayama, and Lipsky (72) have reported observations on the absorption and fluorescence spectra of benzene in vapor phase and various solvents. Their data are consistent with the trend of increased broadening of bands and loss of structure with solvent polarity. Perfluorinated solvents exert the least effect, the spectra retaining much of the fine structure of the vapor phase. Figure 1 shows the data of Lipsky and co-workers (72) for vapor phase benzene, and for solutions in hexane and perfluorohexane.

The influence of environmental perturbations on the degree of allowedness of the symmetry-forbidden 0-0 band has been
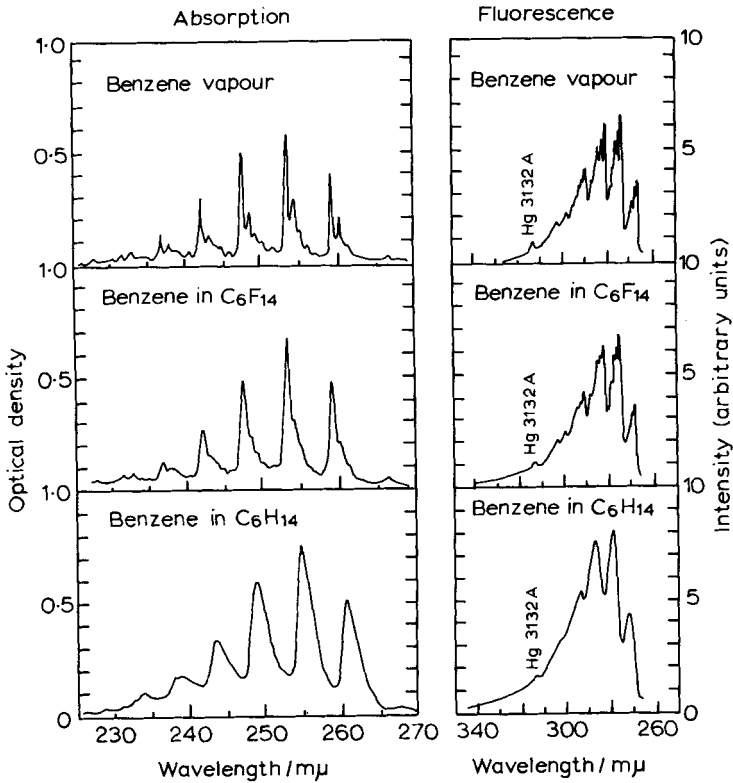
FIGURE 1. Absorption and emission spectra
for benzene in (a) vapor phase, (b) per-
fluorohexane, (c) hexane. (Lawson et al.[72]).

thoroughly investigated. The first study on the effect was car-
ried out by Ham (73) using benzene dissolved in hydrocarbon
glasses with addition of carbon tetrachloride in various propor-
tions. Bayliss and Hulme (74) also found a new absorption band
appearing in benzene dissolved in carbon tetrachloride, chloro-
form and water, among other solvents, and a more detailed study
was later carried out by Kanda (75) and by Bayliss and Cant (76).
Platt (77) in a review concerned with the location of the second
triplet state of benzene called these Ham bands and suggested
that they arise from the spin forbidden $^3E_{1u} \leftarrow {}^1A_{1g}$ transition,
a view shared by other authors (78,79). Robinson (80) proposed

that the Ham bands in carbon tetrachloride solid matrices are due
to intensity borrowed from the solvent and have nothing to do
with the $^3E_{1u} \leftarrow {}^1A_{1g}$ transition. The correctness of this view
was conclusively shown by Leach et al. (5), who have resolved
the 0-0 band of benzene fluorescence in presence of CCl_4 at
77°K, finding a mirror image of the $^1B_{2u} \leftarrow {}^1A_{1g}$ absorption
including the Ham bands. Further absorption studies on Ham
bands have been reported by other authors (82-86) and evidence
for environmental enhancement of the 0-0 bands of fluorescence
and phorphorescence is also available (87-90).

A detailed investigation of the solvent effects on the in-
tensity of the 0-0 bands of C_6H_6 and C_6D_6 was recently carried
out by Cundall and Pereira (91-93) by measuring fully corrected
fluorescence and phosphorescence spectra, fluorescence and
phosphorescence lifetimes, triplet yields, and electronic absorp-
tion spectra at various temperatures in a large variety of sol-
vents. It was found that the rate constants for fluorescence
and intersystem crossing are only slightly affected by solvent
while the rate constant for the nonradiative process from S_1 to
S_o is solvent dependent, in agreement with results obtained by
Eastman and Rehfeld (70). A good correlation was established
between k_{ICM} and the extent of solvent-induced 0-0 band inten-
sity in both absorption and fluorescence bands (91). A solvent
dependence on the rate constant k_{ICM} was also found by Luria,
Ofran, and Stein (94), who have measured fluorescence lifetimes
of benzene in a series of polar and nonpolar solvents and the
trend obtained is in good agreement with results of Cundall and
Pereira (91). A similar correlation between the solvents en-
hancing the fluorescence 0-0 band and the efficiency of the in-
ternal conversion from $^1E_{1u}$ to $^1B_{2u}$ was reported by Lawson et
al. (72). This shows that solvents which give a higher proba-
bility of the nonradiative transition from S_3 to S_1 also increase
the nonradiative transition from S_1 to S_o. In Fig. 2 the fully
corrected fluorescence spectrum of benzene solutions in methanol
at 77°K and the absorption spectrum at 233°K are represented (91);
a good mirror relationship is displayed, including 0-0 bands
enhanced bands by solvent perturbation. It was also established
by these authors that in the presence of chloroform and carbon
tetrachloride the symmetry-forbidden 0-0 bands are enhanced in
both fluorescence and phosphorescence, while xenon enhances
these bands only in phosphorescence. These effects are illus-
trated at 77°K in Figs. 3 and 4, respectively, for benzene-d_6
in methylcyclohexane + chloroform and for benzene-h_6 in ethanol
and in ethanol + xenon. The extent of enhancement was given for
fluorescence by the ratio Fo/F$_1$ in which Fo represents the peak
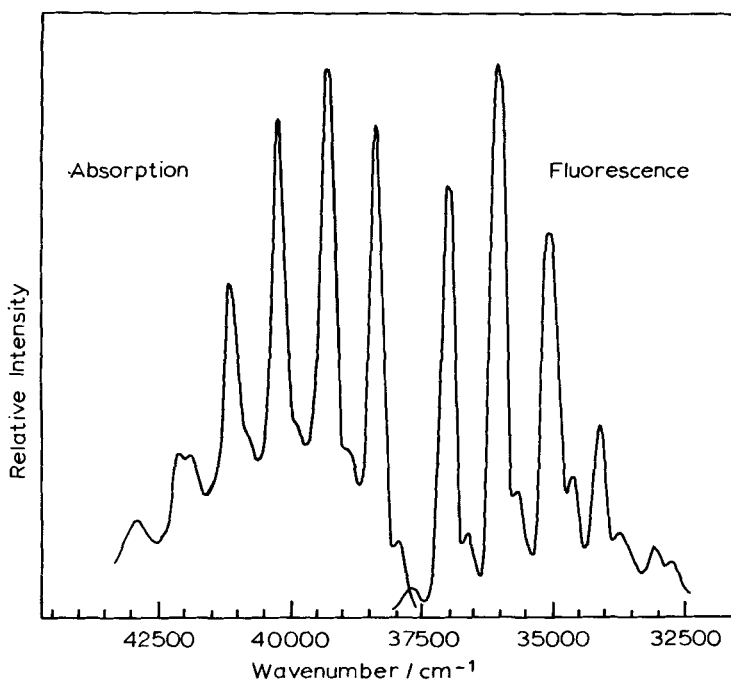
FIGURE 2. Absorption and fully corrected
fluorescence spectra of benzene at 233°K and
77°K, respectively.[92]

height of the 0-0 band and F_1 the peak height of the vibronic
allowed band at the wavenumber $\bar{\nu}_{o-o}-606$ cm^{-1}, and for phosphores-
cence by the ratio Po/P_2, where Po is the peak height of the 0-0
band and P_2 the corresponding peak intensity at about $\bar{\nu}_{o-o}-1500$
cm^{-1}, as shown in Fig. 4. Some of the results obtained from this
type of measurement are indicated in Tables 3 and 4. From phos-
phorescence lifetimes, (τ_P), it was shown by the above authors
that a decrease of τ_P and increase of the ratio of phosphorescence
to fluorescence yield, (χ), parallels the enhancement of the 0-0
phosphorescence band in most of the solvents investigated. The
results were interpreted in terms of a distortion of both the
$^1B_{2u}$ and $^3B_{1u}$ states induced by solvent perturbation, distortion
in the $^3B_{1u}$ state being greater than in the $^1B_{2u}$ state, in agree-
ment with results reported by Nieman and Tinti (58).
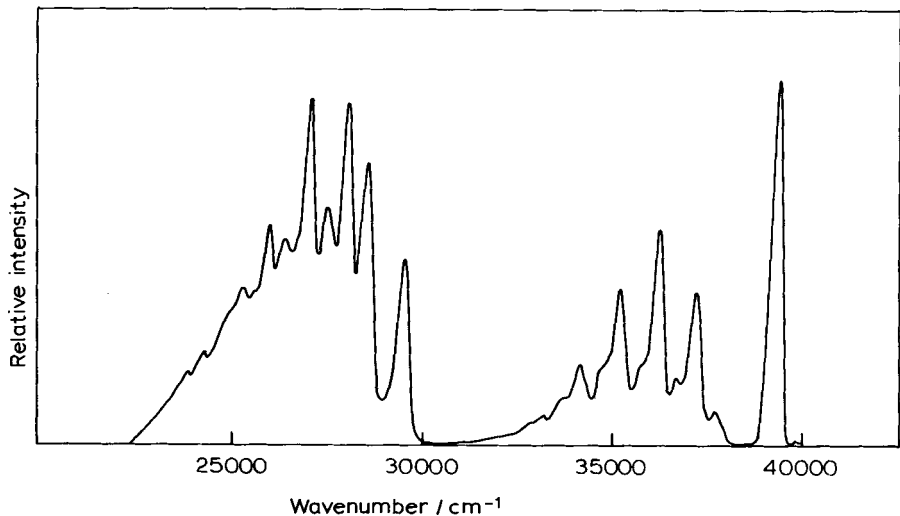
FIGURE 3. Fully corrected spectra (fluorescence and phosphorescence) of benzene in methylcyclohexane + 10% chloroform at 77°K,[92] first-excitation band.

Observations on transitions between S_o and the lowest triplet state are difficult in nonrigid media and it is not possible to say with certainty that this transition is similarly affected by environment.

Nonradiative processes may occur other than through $\pi-\pi^*$ configurations. Other types of state may, as a result of their charge distributions, be more susceptible to interaction with the environment than the emitting π,π^* states.
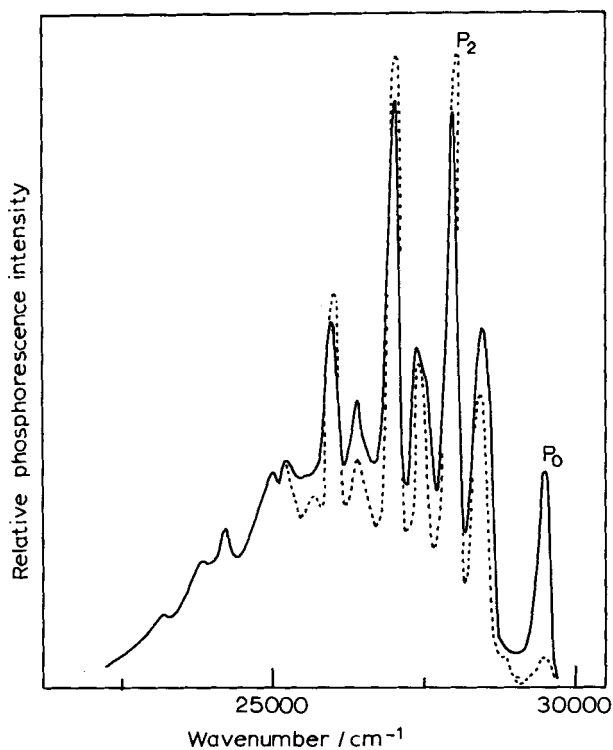
FIGURE 4. Fully corrected phosphorescence
spectra of benzene in ethanol (----) and in
ethanol + xenon (———) at 77°K.[92]

VI. THE $S_1 \leftrightarrow S_0$ RADIATIVE TRANSITION

The $^1B_{2u} \leftarrow {}^1A_{1g}$ absorption transition has been well studied
and is discussed in the previous sections. Theory predicts an
integrated absorption intensity independent of temperature. Be-
low room temperature, Eastman and Rehfeld (70) found a similar
absorption spectrum for benzene in 2-methyl-1-propanol at 25°C
and at -140°C, that at low temperature being sharper and better
resolved. Above room temperature there is a rather more marked
effect on peak intensity (95) accompanied by peak broadening and
the expected increase in hot band intensity at 260 nm. This is

TABLE 3.   Intensity of forbidden bands (fluorescence and phos-
phorescence) for benzene-h_6 in various solvents at 77°K (91-93).

Solvent	F_0/F_1	P_0/P_2
Methylcyclohexane	0.050	0.074
Methylcyclohexane + 10% $CHCl_3$	0.155	0.530
Methylcyclohexane + 7% C Cl_4	0.094	0.280
Ethanol	0.076	0.070
Methanol	0.077	0.060
Acetonitrile	0.110	-
Ethanol + xenon (∿0.8M)	-	0.380

TABLE 4.   Intensity of forbidden bands (fluorescence and phos-
phorescence) for benzene-d_6 in various solvents at 77°K (91-93).

Solvent	F_0/F_1	P_0/P_2
Methylcyclohexane	0.072	0.040
Methylcyclohexane + 10% CHC_3	0.234	0.470
Methylcyclohexane + 20% $CHCl_3$	0.260	0.440
Methylcyclohexane + 10% CCl_4	0.146	0.260
Ethanol	0.082	0.047
Methanol	0.076	0.060
Acetonitrile	0.100	-
Ethanol + xenon (∿0.8H)	-	0.26

well illustrated in Figs. 5 and 6. The changes are brought about
by variations in energy distribution within the system, and the
integrated intensity is approximately constant (70,94). At very
high temperatures the spectrum becomes very broad as observed in
shock wave experiments (96).

The $^1B_{2u} \leftarrow {}^1A_{1g}$ symmetry forbidden emission transition ob-
served in all three phases, results from vibrational perturba-
tion of the ground state. The fluorescence spectrum follows the
changes in resolution, shape, and frequency with environment,
observed in the absorption spectrum. It is, in all cases, a fair
mirror image of the absorption spectrum, demonstrating that emis-
sion occurs from the electronic state created by absorption in the
260 nm region. Fluorescence intensity varies considerably with
environment (see Tables 5 - 11), though as will be shown, this
results from media effects on competitive processes, rather than
on the probability of emission.
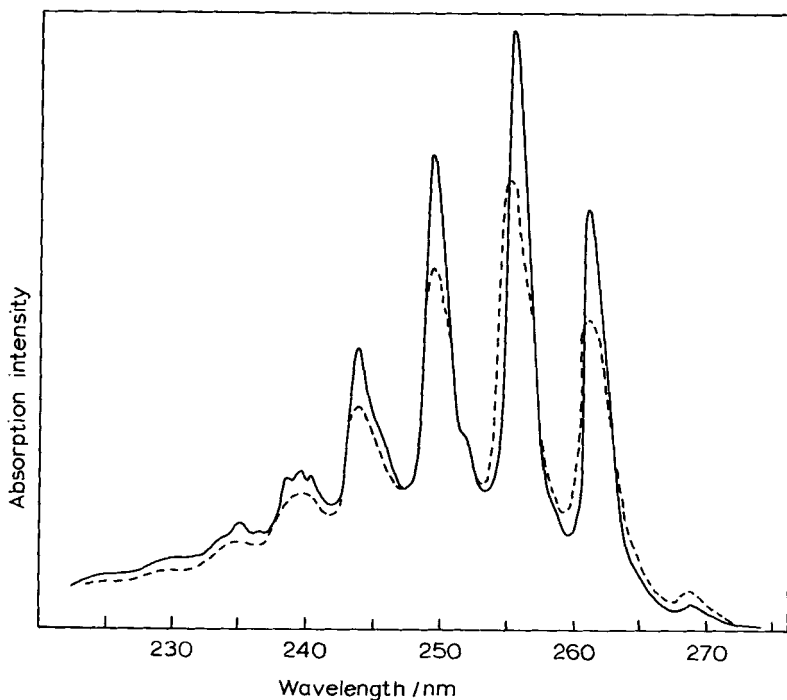
FIGURE 5. Variation in absorption spectrum (first
band) with temperature for benzene in cyclohexane,
11°C (———) 75°C (----) (Robinson[95]).
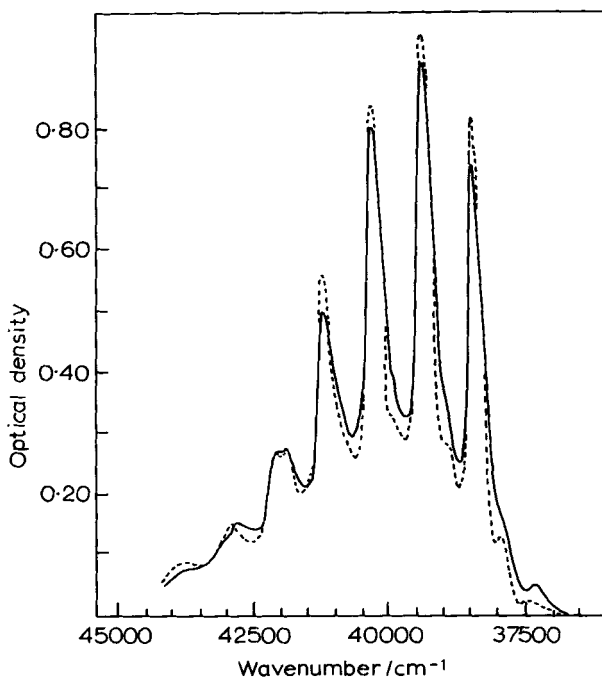
FIGURE 6.   Absorption spectra of benzene in
methanol at room temperature (———) and at
-40°C (----)[92].

     One of the most significant advances in spectroscopic
techniques in recent years has given data on single vibronic
level fluorescence yields and associated emission lifetimes of
individual vibronic levels.   Details of the experimental technique
and of the results achieved have been reviewed by Parmenter (97).
Parmenter and Schuyler (98,99) succeeded in recording fluorescence
spectra from low pressure (<0.2 torr) benzene vapor excited with
a band pass sufficiently small ($\sim$ 40 cm^{-1}) to ensure that single
vibrational levels of the $^1B_{2u}$ state were created.   In the lower
levels the spectra recorded were sharp and structured, as would
be expected in a system in which collisional redistribution of
energy prior to fluorescence does not occur.   At higher energy
excitation the emission spectra become more diffuse, and the
fluorescence intensity drops to zero when levels of excess energy

TABLE 5.   Monomer fluorescence yields in the gas phase.

ϕF	Isomer	Temp.($^{\circ}$C)	Conditions/Remarks	Ref.
0.21	C_6H_6	30	2 torrs, 254 nm excitation	(100)
0.32	C_6H_6	30	0.077-0.12 torr λ_{exc} 254 nm	(101)
0.39	C_6H_6	30	0.01-0.4 torr λ_{exc} 254 nm	(102)
0.22	C_6H_6		For zeroth level	(98)
0.27	C_6H_6		For 1st e_{2g} band low-pressure vapor	(98)
0.18	C_6H_6			(103)
0.39	C_6H_6		P $\geq 10^{-2}$ torr λ_{exc} 254 nm	(104)
0.18	C_6H_6	25	P > 10 torrs λ_{exc} 254 nm	(105)
0.31	C_6H_6	30	P 10-32 torrs λ_{exc} 264 nm	(100)
0.23	C_6D_6	25	P 10 torrs λ_{exc} 254 nm	(105)
0.53	C_6D_6	30	P 4-15 torrs λ_{exc} 264 nm	(100)
0.26	C_6D_6	30	P 5.2 torrs λ_{exc} 254 nm	(100)
0.35	C_6D_6		Low-pressure-single level fluorescence, zeroth level	(106)

> 2500 cm^{-1} are excited. Quantum yields for the emission from the various levels were estimated from the established high pressure yield of 0.18. Data are given in Tables 5 and 6.

Further quantum yield measurements (111) and emission life-times (111-113,115) have also been reported which demonstrate that the radiative transition probability from a vibronic state is determined by the combination of vibrational modes that have been excited. The transition rates that may be of interest in comparing data from all three phases are, of course, those from the lower levels of S_1, since relaxation in higher-pressure gases and condensed media will lead to these states. The data of Spears and Rice (111) show that the emission probability from the levels 0, 6^116^1 and 1^1 are 2.2 x 10^6s^{-1}, 3.4 x 10^6s^{-1},

TABLE 6.   Monomer fluorescence lifetimes in the gas phase.

τ_F/ns	Isomer	Conditions	Ref.
60	C_6H_6	High pressure (5-40 mm) λ_{exc} 230-280nm	(107)
80	C_6H_6	High pressure λ_{exc} 259 nm	(108)
77	C_6H_6	λ_{exc} 260, extrapolated to zero pressure	(109)
80±10	C_6H_6	3-10 torrs, λ_{exc} 254 nm	(110)
100	C_6G_6	-Zeroth level ⎫	(111)
79	C_6H_6	1st e_{2g} level ⎬ low pressure	
90	C_6H_6	-Zeroth level ⎫	(112)
80	C_6H_6	-1st e_{2g} level ⎬ low pressure	(112)
72	C_6H_6	High pressure λ_{exc} 247-266 nm	(113)
164	C_6D_6	Zeroth level ⎫	(113)
125	C_6D_6	-1st e_{2g} level ⎬ low pressure	(113)
92	C_6D_6	High pressure limit λ_{exc} 247-266	(113)
200	C_6D_6	Zeroth level	(113)
95	C_6D_6	High pressure (5-40 torrs) λ_{exc} 230-280	(106)
72	C_6H_6	50 torrs indep. of λ_{exc} 245-270 nm	(114)
92	C_6D_6	50 torrs indep. of λ_{exc} 245-270 nm	(114)

$3.4 \times 10^6 s^{-1}$, and $2.5 \times 10^6 s^{-1}$, respectively. Data from the comparable transitions (106) in C_6D_6 give the values $1.75 \times 10^6 s^{-1}$, $2.9 \times 10^6 s^{-1}$, $3.3 \times 10^6 s^{-1}$, and $3.0 \times 10^6 s^{-1}$, respectively. In benzene-d_6 the sharp drop in quantum yield with energy in excess of zero point level for the transition is noted (106) in a similar region to that for C_6H_6, about 3500 cm^{-1} above the 0-0 band.

With increase in benzene (or added gas) pressure, the rate of collisional redistribution of excitation energy becomes

TABLE 7. Rate constants for fluorescence of benzene-h_6 and benzene-d_6, as a function of temperature assuming a non-quenchable internal conversion process.

	$T(^{\circ}C)$	$k_F \times 10^6 (s^{-1})$
	25	2.76
	40	2.79
	50	2.84
Benzene-h_6	60	2.93
	70	3.06
	80	3.24
	100	3.72
	25	2.85
	40	3.09
Benzene-d_6	50	3.30
	60	3.51
	70	3.78
	80	4.42
	100	4.98

competitive with the fluorescence rate to an extent which depends upon the total pressure of the system. Quantum yield and emission lifetime measurements reflect the nonequilibrium distribution of excited molecules in the medium-pressure range; for example, for excitation of C_6H_6 at 254 nm, yields of (100) 0.21 (for 2 mm pressure) and a negative dependence upon increasing gas pressure have been reported. A similar dependence upon gas pressure is evident for C_6D_6; again for excitation at 254 nm, yields of 0.33 (100), 0.28 (100), 0.26 (100), and 0.23 (116) have been reported for pressures of 1.2 3.0, 5.2, and >10 torrs, respectively. Also the work of Poole (100) has demonstrated that the yield is a function of excitation wavelength, dropping to zero in both benzene and the per-deutero derivative at excitation wavelengths of 240 nm and below.

TABLE 8.   Monomer fluorescence yields for benzene in solution.

ϕ^O_{FM}	Isomer	Temp. (°C)	Solvent	Remarks	Ref.
0.060	C_6H_6	25	Hexane	Relative to toluene	(119)
0.052	C_6H_6	25	Me-cyclohexane		(119)
0.061	C_6H_6	25	Cyclohexane		(70)
0.046	C_6H_6	25	Me-cyclohexane		(70)
0.058	C_6H_6	25	Hexane		(70,120)
0.060	C_6H_6	25	Hexane		(121)
0.061	C_6H_6	25	Cyclohexane		(122)
0.053	C_6H_6	AMB	Hexane		(123)
0.050	C_6H_6	20	Hexane		(124)
0.071	C_6H_6	25	Me-cyclohexane	Relative to ϕ^O_{FM} (DPA)=1.0	(125)
0.070	C_6H_6	RMT	Cyclohexane		(126)
0.066	C_6D_6	25	Cyclohexane		(126)
0.042	C_6D_6	24	Me-cyclohexane		(127)
0.042	C_6H_6	RMT	Ethanol		(128)
0.040	C_6H_6	25	Ethanol		(119)
0.025	C_6H_6	25	Acetonitrile		(119)
0.029	C_6H_6	25	Methanol		(119)
0.027	C_6H_6	25	Methanol		(70)
0.033	C_6H_6	25	Ethane		(70)
0.025	C_6H_6	25	Acetonitrile		(119)
0.006	C_6H_6	25	Water		(129,130)
0.0058	C_6H_6	25	Water		(70)
0.065	C_6H_6	25	Per-fluoro-n-hexane		(91)

TABLE 9. Monomer fluorescence emission lifetimes for benzene in solution.

τ_{FM} (ns)	Isomer	Temp. (^{o}C)	Solvent	Ref.
29	C_6H_6	RMT	Cyclohexane	(126)
24	C_6H_6	20	Hexane	(131)
26	C_6H_6	RMT	Cyclohexane	(132)
27.5	C_6H_6	24	Hexane	(133)
29.5	C_6H_6	25	Cyclohexane	(134)
32	C_6H_6	20	n-Nonane	(135)
27.9	C_6H_6	25	Me-cyclohexane	(136)
45	C_6H_6	RMT	Hexane	(137)
34	C_6H_6	25	Cyclohexane	(119)
30	C_6H_6	25	Me-cyclohexane	(119)
33.6	C_6H_6	25	Hexane	(138)
26.6	C_6D_6	25	Cyclohexane	(125)
33	C_6D_6	22	Cyclohexane	(139)
28	C_6H_6	25	Cyclohexane	(139)
30	C_6D_6	25	Me-cyclohexane	(127)
31	C_6H_6	RMT	Ethanol	(121)
26	C_6H_6	25	Ethanol	(119)
20	C_6H_6	25	Methane	(119)
2.2	C_6H_6	25	Water	(129)
15	C_6H_6	25	Acetonitrile	(119)

TABLE 10.   Fluorescence yields for benzene in the solid phase.

ØFM	Isomer	Temp. (°K)	Solvent	Remarks	Ref.
0.21	C_6H_6	77			(148)
0.26	C_6H_6	77	EPA	± 10%	(149)
0.20	C_6H_6	77	EPA		(150)
0.22	C_6H_6	173	Benzene		(151)
0.29	C_6H_6	77	Crystal		(152)
0.22	C_6H_6	77	EOA	Ether/isooctane/ alcohol	(144)
0.19	C_6H_6	77	EPA		(153–155)
0.27	C_6D_6	77	EPA		(153–155)
0.21	C_6H_6		n–Hexane		(120)
0.18	C_6H_6		Methanol		(120)
0.17	C_6H_6	30	30/70 iso but/isopent	Limiting low- temp. values	(120)
0.21	C_6H_6		EPA		(120)

TABLE 11.   Fluorescence emission lifetimes for benzene in the solid phase.

τ_F (ns)	Temp. (°K)	Solvent	Remarks	Ref.
84	173	Benzene	No phosphorescence detected	(151)
120±6	77	Me–cyclohexane		(93)
115±5	77	Ethanol		(93)

It is considered that pressures of 10 torr or greater are required for complete collisional deactivation to an equilibrium distribution of energy between levels prior to emission. Under these conditions, the fluorescence yield appears independent of further increases in pressure, and achieves a value of 0.18 (100,103,105,116) for all first singlet band excitation wavelengths in excess of 247 nm.

Fluorescence yields for C_6H_6 and C_6D_6 decrease (100,105) with increasing temperature; the data of Dunnicliff (105) are presented in Fig. 7 for $2.5 \times 10^{-4}M$ and $7.1 \times 10^{-4}M$ benzene between 20 and 140°C.

Emission lifetimes for benzene with vapor phase are subject to similar variations with pressure and excitation wavelength as are fluorescence yields. Data are collected in Table 6 and can be seen to show considerable variation with source and experimental technique. Recent measurements, using a single-proton counting technique (114) have shown the emission lifetimes of high pressure C_6H_6 and C_6D_6 to be 77 and 92 ns, respectively, at 25°C. The temperature dependence of the fluorescence lifetime is also shown in Fig. 7.
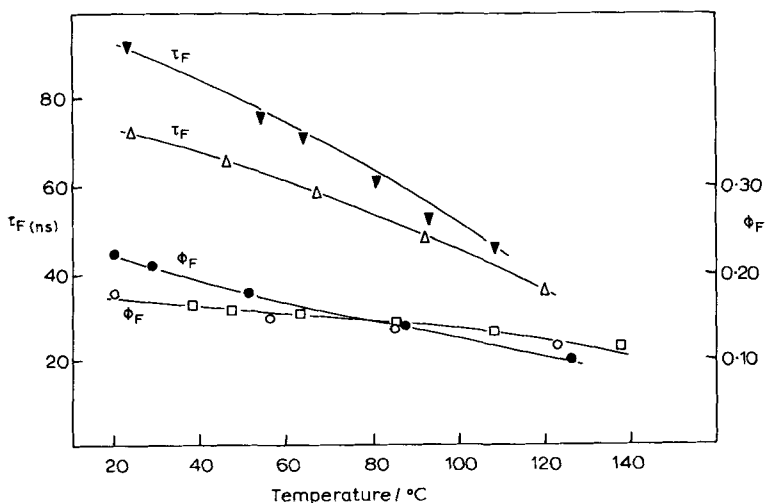

FIGURE 7. The variation in ϕ_F and τ_F for vapor-phase benzene as functions of temperature (Dunnicliff[105] and Lockwood[114]). The filled points are for C_6D_6. The open points are for C_6H_6.

At high pressures gaseous system most closely resemble the situation in condensed media, and it is instructive to determine the radiative rate constant for this system, and its variation with temperature. Assuming that internal conversion from S_1 is a nonquenchable process which occurs prior to vibrational relaxation from a nonequilibrated state and using results of $\emptyset_F$ and $\emptyset_T$ determined by Cundall and Dunnicliff (105) and values of τ_F due to Lockwood (114), the calculated k_F values are presented in Table 7 for both C_6H_6 and C_6D_6. The similarity of rate constants for the protonated and deuterated molecules indicates that the large differences in yield and lifetime for the two isomers are the result of an isotope effect on a nonradiative transition.

In the medium pressure region, it has been suggested that fluorescence in the collisionally equilibrated gas phase system results from two (117) or three (118) vibrational levels of S_1. Whether this be the case, and if emission involves a multistep cascade through vibrational levels, it seems likely from considerations of the levels initially populated, the rates of vibrational deactivation, and the Boltzmann distribution of levels in the equilibrated system, that emission is dominated by transitions from the zeroth level. This is borne out by comparison of high-pressure values of k_F with zeroth-level transition probability discussed previously; $2.8 \times 10^{-6}s^{-1}$ and $2.2 \times 10^6 s^{-1}$, respectively, for C_6H_6 at $25^{\circ}C$; though the discrepancy is greater for C_6D_6 for which the values are $2.9 \times 10^6 s^{-1}$ and $1.7(5) \times 10^6 s^{-1}$.

In solution, the quantum yields and lifetimes for fluorescence emission for benzene are dependent upon solvent (see Tables 8 and 9, and more detailed data in reference 70) and temperature (140), but yield has been shown (141-145) to be independent of excitation wavelength within the first absorption band (λ exc > 230 nm). The observed variations arising from different exciting sources and experimental methods, in yield and lifetime for similar and even identical solvents reflect the difficulty experienced in obtaining reliable fluorescence data. Despite this unfortunate limitation, some trends may be discerned. In general, quantum yields and lifetimes tend to be larger in nonpolar solvents (91, 119), although in all cases these quantities are much smaller than in the gas phase. There appears to be no significant isotope effect on either parameter, contrary to expectation from a comparison with gas phase data (107,112).

The oscillator strength for the $S_1 \leftarrow S_0$ transition is almost independent of solvent (70,74,94), and it might thus be expected that the effect of solvent on the radiative probability would be slight. Cundall and Pereira (91,119) have reported measurements of k_{FM} in polar solvents, nonpolar solvents, and in particular perfluoro-n-hexane (in which solvent the similarity of

spectral characteristics to those in vapor phase show that the solute-solvent interactions are minimal). It is found that although slight variations in k_{FM} with solvent occur, the variations are not accounted for by considerations of solvent polarity, and it may well be that k_{FM} is independent of solvent; lying within the range $1.5 - 1.8 \times 10^6 s^{-1}$. The variation of $\emptyset_F$ and τ_F with solvent must, therefore, be the result of a medium effect on the nonradiative decay process. The difference between mean monomer transition probability in a range of solvents, and values from high-pressure and zeroth-level gas phase data is significant: $1.5 - 1.8 \times 10^6 s^{-1}$ compared with $2.2 \times 10^6 s^{-1}$ and $2.8 \times 10^6 s^{-1}$. Application of the disputed refractive index, n^2, correction further increases the divergence between these data; while the theoretical value for k_{FM} ($2.5 \times 10^6 s^{-1}$) derived using the Strickler-Berg equation, neglecting n^2 is in close agreement with the gas phase data. The phase effect may be the result of uncertainties in measurement of various parameters, or, more probably interactions in the condensed phase which are not explained by the n^2 relationship. Reported data on C_6D_6 are less extensive than for C_6H_6 and contradictory. The data of Berlman (126) for $\emptyset_F$ and τ_F indicate that $k_F(C_6D_6)$ is larger than that for the perprotonated species. The data used by Sandros (146) and Helman (139) provide conclusions intermediate between those of Berlman (126), and those of Cundall, Olgivie, and Robinson (127), who reported a value for $k_F(C_6D_6)$ lower than that of C_6H_6. Rice and co-workers noted the similar trend in radiative lifetimes of the zeroth vibrational level in fluorescence (106,111), and attributed the effect to a greater purity of the electronic levels in perdeuterobenzene, which is also mirrored by changes in oscillator strength with isotopic substitution (86).

It was noted earlier that there was a small temperature effect on k_F in the gas phase. A similar effect is also observed in solution (94,119). Although in nonpolar solvents the effect is relatively small (119,136,147), it is accentuated in more polar environments (119). The effect is smaller for C_6D_6.

Reliable fluorescence quantum yields and lifetimes in the solid phase are difficult to determine, and accurate data are sparse (see Tables 10 and 11). It is well established that fluorescence and lifetimes of dilute solutions of benzene increase with decreasing temperature (8,119). In a recent study of similar molecules (156-158), it was shown that the increase in both $\emptyset_F$ and τ_F is smooth, and that both these quantities tend towards a limiting value at low temperature. An analysis of the temperature dependence of the two parameters for benzene in a variety of solvents (119) has indicated that the limiting values for both should be reached at a temperature well above $77^{\circ}K$, since the controlling variable is the radiationless Channel III process(es)

which has a solvent dependent activation energy characteristically in excess of 0.2 eV. The term "Channel III" has been introduced to describe the process or processes other than fluoresence or triplet state formation which lead to the disappearance of $^1B_{2u}$ state (see Section VIII). Measurements at 77^OK are thought to provide the limiting low-temperature values for the two fluorescence parameters.

Eastman (120) has reported limiting yields of 0.21, 0.18, 0.17, and 0.21 for benzene in n-hexane, methanol, 30/70 isobutanol/ isopentane, and EPA, respectively. The yields are seen to be solvent dependent and determination of k_F requires emission lifetimes in identical media. Such are not available though limiting values of 120 and 115 ns have found (93) for benzene in methylcyclohexane and ethanol, respectively, at 77^OK. Making the crude assumption that media effects are due to differences in solvent polarity we can calculate radiative rate constants of 1.75 x 10^6s^{-1} for hydrocarbon solvents and 1.6 x 10^6s^{-1} for alcohol solvents.

The similarity of these values to those mentioned earlier for room temperature solution work leads to the conclusions that the radiative rate constant is independent of temperature (below ambient) and that the difference between gas phase and condensed phase data is a real effect resulting from some molecular interaction not accounted for by the n^2 correction which conventional theory requires.

VII.   THE $S_1 \rightarrow$ TRIPLET RADIATIONLESS TRANSITION

From analysis of fluorescence yields and lifetime measurements on emission from single vibronic levels (98,99,111-113,115) "rate constants" for total radiationless decay may be determined. These are also dependent upon vibrational level involved. Spears and Rice (111) have reported nonradiative lifetimes of 128, 108, 104, 105 ns, respectively, for the levels considered previously. The fluorescence "cut off" region, noted in these reports, suggests, in agreement with several other indications discussed in Section VIII, that radiationless $S_1 \rightarrow S_0$ decay proceeds via a highly vibrationally energetic level of S_1. The report of Rice and co-workers (106) on benzene-d_6 in this type of experiment shows that the nonradiative transition from S_1 is affected by deuteration to a greater extent than the fluorescence transition; the nonradiative lifetimes of the four comparable levels being 565, 345, 300, and 340 ns, respectively.

Triplet quantum yields for benzene vapor in collisionally deactivating systems have been estimated by a number of techniques (Table 12), involving sensitized isomeration, decomposition, or

TABLE 12. The S_1 triplet transition for benzene in the gas phase.

$\emptyset_T$	Isomer	Temp. ($^{\circ}$C)	Conditions	Technique	Ref.
0.72	C_6H_6	Room	2-19 torrs λ_{exc}254nm	Butene-2	(159)
0.72	C_6H_6	Room	7-26 torrs λ_{exc}252-67nm	Butene-2	(160)
0.71	C_6H_6	Room	10 torrs λ_{exc}252nm	Ketene	(161)
0.71	C_6H_6	Room	Cyclobutanone	Cyclo-butanone	(162)
0.79	C_6H_6	Room		Pyrazine	(163)
0.63	C_6D_6	Room	2-19 torrs λ_{exc}254 nm	Butene-2	(159)
0.71	C_6H_6	Room	> 10 torrs λ_{exc}=254 nm	Butene-2	(105)
0.70	C_6H_6	40	> 10 torrs λ_{exc}=254 nm	Butene-2	(105)
0.68	C_6H_6	60	> 10 torrs λ_{exc}=254 nm	Butene-2	(105)
0.65	C_6H_6	80	> 10 torrs λ_{exc}=254 nm	Butene-2	(105)
0.63	C_6H_6	100	> 10 torrs λ_{exc}=254 nm	Butene-2	(105)
0.61	C_6D_6	Room	> 10 torrs λ_{exc}=254 nm	Butene-2	(105)
0.52	C_6D_6	50	> 10 torrs λ_{exc}=254 nm	Butene-2	(105)
0.46	C_6D_6	70	> 10 torrs λ_{exc}=254 nm	Butene-2	(105)
0.37	C_6D_6	100	> 10 torrs λ_{exc}=254 nm	Butene-2	(105)

luminescence of additives. It is to be expected that the overall intersystem crossing efficiency is dependent upon the extent of collisional deactivation and redistribution of energy following excitation. The presence of appreciable quantities of added gas, which may arise because of the presence of the triplet monitor, and the use of benzene pressures in excess of 10 torrs ensure that the yields of triplets reported for gas phase systems result from intersystem crossing from thermally equilibrated range of levels in S_1. Of the many triplet monitors used, it is widely believed that butene-2 effectively quenches only the triplet state.

Dunnicliff (115) has shown that the olefin also quenches singlet S_1 benzene, but only with a bimolecular rate constant of 2.2 x 10^8 $M^{-1}s^{-1}$, so at the olefin concentrations commonly used for triplet scavenging, singlet state quenching is negligible compared with that of the triplet state.

Noyes and Harter (160) obtained evidence of a decrease in triplet yield with decrease of excitation wavelength. A limiting high-pressure yield of 0.71 at room temperature after excitation at 254 nm is now well established. The observed isotope effect is large; with corresponding high-pressure limit values of 0.63 (159) and 0.61 (105) reported for C_6D_6, under the same conditions. Using the emission lifetime measurements of Lockwood (114), inter-system crossing rate constants (for heavy and light benzene) of 7.9 x $10^6 s^{-1}$ and 11 x $10^6 s^{-1}$ are obtained assuming a nonquenchable internal conversion also occurs. For this transition, the crude assumption that the high-pressure rate constant is dominated by the contribution from the zeroth level may not be valid. As dis-cussed earlier, transition may be to either or both of the $^3E_{1u}$ and $^3B_{1u}$ states. Transition to $^3B_{1u}$ has first-order spin-orbit allowedness, but the rate constant may be reduced by the small Franck-Condon overlap factor resulting from the 1.1 eV energy gap between states. Transition to $^3E_{1u}$ requires vibronic coupling. The positions of the three states in C_6D_6 relative to the equi-valent states in C_6H_6 are not accurately known, though spectro-scopic evidence (39,164,165) suggests that the energy spacings are slightly increased (200 cm^{-1}) by deuteration. In addition, deu-terium substitution reduces the energy separation of the vibra-tional levels (166-169). There is some confusion concerning whether deuterium atom substitution affects (170) the radiation-less $T_1 \rightarrow S_0$ transition or otherwise. Because of this uncertainty, it is probably unacceptable to seek similarities between the mea-sured rate constant in high-pressure gases and in the nonradiative decay rates of the zeroth vibrational levels of S_1 states of C_6H_6 and C_6D_6.

Considerable data are available for triplet yields of ben-zene in dilute solutions of different solvents (see Table 13). In the main, two techniques have been used; sensitized phosphor-escence of biacetyl, sensitized cis-trans isomerization of butene-2, octene-2, and stilbene. All yield comparable results. In saturated hydrocarbon solvents at room temperature, the triplet yield for C_6H_6 is found to be about 0.24 ± 0.01. There is a sol-vent dependence of this quantity, the yield dropping to 0.15 in ethanol, 0.13 in methanol, and 0.09 in acetonitrile (91). In determining the effect of environment on the rate constant con-trolling intersystem crossing, values for emission lifetimes in the various systems are needed. These are, as mentioned pre-viously, often unreliable. Cundall and Pereira (91) have reported

consistent data which give the variation in k_{ISCM} (= ϕ_T/τ_F) with solvent. It is found that, though differences between solvents occur, there is no consistent trend with solvent polarity, and we can consider k_{ISCM} to be independent of solvent within the range of approximately $7(\pm 1) \times 10^6 s^{-1}$. Further, there appears to be little isotopic effect on k_{ISCM} since a rate constant of $8.7 \times 10^6 s^{-1}$ has been reported for C_6D_6 (127) in methyl-cyclohexane at room temperature compared with $8.0 \times 10^6 s^{-1}$ for the perprotonated solute (91).

The variation of k_{ISCM} with temperature for C_6H_6 in cyclohexane (182) is more marked than that for C_6D_6 (127) similar to the trends noted in gas phase studies (105). It is erronous to fit this temperature dependence to a simple Arrhenius function, since the yield of phosphorescence at low temperature shows a substantial triplet production in the solid phase. More realistically, the room temperature process may be viewed as the sum of two intersystem crossing steps to the two lowest triplet states. One process being temperature independent ($\to {}^3B_{1u}$?) and the other temperature dependent ($\to {}^3E_{1u}$?).

Estimation of triplet yields from benzene in the solid phase presently requires several approximations, since the available triplet monitoring methods do not function in solid media. Pereira (93) has shown that the quantum deficit $1-(\phi_F + \phi_T)$ may be assigned in benzene although not necessarily to substituted benzene derivatives, to a single process, and that $(\phi_F + \phi_T)$ approaches unity with decreasing temperature. In this way, the deficit $(1 - \phi_F)$ may be assigned to ϕ_T at low temperatures. Using the emission yields and limiting low temperature lifetime data from Tables 10 and 11, together with the solvent effect assumption noted previously, we may calculate rate constants of 6.6×10^6 and $7.1 \times 10^6 s^{-1}$ for intersystem crossing in hydrocarbon and polar media, respectively.

It is seen that the rate constants for intersystem crossing are broadly, that is, within ± 10 percent, independent of molecular environment. We must conclude that the significant differences noted in fluorescence and triplet yields and lifetimes, with phase, must be the result of an effect on the "hidden" $S_1 \to S_0$ decay process.

VIII.   THE $S_1 \to S_0$ RADIATIONLESS TRANSITION

Evidence that decay of the first excited singlet state may occur via a nonradiative process which depends on the vibrational energy and probably does not involve the lower triplet states of the π manifold comes from various types of experiment:

TABLE 13. Triplet yields in the solution phase.

$\emptyset_T$	Isomer	Temp. (°C)	Conditions	Monitor	Ref.
0.24	C_6H_6	29	Pure benzene	Piperylene	(172)
0.57	C_6H_6	25	Pure benzene	Butene-2	(173)
0.60	C_6H_6	25	Pure benzene	Octene-2	(174)
0.56	C_6H_6	24	Pure benzene	Butene-2	(175)
0.58	C_6H_6	25	Pure benzene	Stilbene	(176)
0.71	C_6H_6	25	Pure benzene	Octene	(177)
0.24	C_6H_6	24	0.11 2M cyclohexane	Butene-2	(147)
0.25	C_6H_6	26	6.10^{-2}M Me-cyclohexane	Butene-2	(178)
0.25	C_6H_6	20	Dil. cyclohexane	Biacetyl	(146)
0.24	C_6H_6	22	Dil. Me-cyclohexane	Octene	(177)
0.23	C_6H_6	25	Dil. cyclohexane	Butene-2	(91)
0.24	C_6H_6	25	Dil. Me-cyclohexane	Butene-2	(91)
0.15	C_6H_6	25	Dil. ethanol	Butene-2	(91)
0.13	C_6H_6	25	Dil. methanol	Butene-2	(91)
0.09	C_6H_6	25	Dil. acetonitrile	Butene-2	(91)
0.07	C_6H_6	25	Dil. water	Butene-2	(91)
0.47	C_6H_6	24	0.IM cyclohexane	Butene-2	(175,178)
0.39	C_6H_6	25	0.3M cyclohexane	Flash photolysis	(179)
0.18	C_6H_6	25	Dil. cyclohexane	Stilbene	(180)
0.23 (5)	C_6D_6	25	Dil. Me-cyclohexane	Butene-2	(178)
0.24	C_6D_6	20	Dil. cyclohexane	Biacetyl	(181)
0.25	C_6D_6	25	Dil. cyclohexane	Butene-2	(127)
0.24	C_6H_6	25	Dil. perfluorohexane	Butene-2	(91)

1. The decrease in quantum yield for $S_1 \rightarrow S_0$ fluorescence with increasing excitation energy has been reported for gas phase (142), liquid phase (141,143,183), and solid phase (144) benzene systems. The decrease in yield shows that the onset of an additional competitive decay process, occurs at an energy above S_1 of the order of 0.3 eV.

2. Low-pressure, narrow band pass excitation studies have shown (98,99,111-113) that the fluorescence yields from single excited vibrational levels of S_1 drop sharply to zero in region of 0.31 eV above the zeroth level of the $^1B_{2u}$ state. The effect is also noted in the perdeuterated molecule (106).

3. Callomon and co-workers (27) report the onset of spectral diffuseness in the $S_0 - S_1$ absorption spectrum of benzene vapor at a level approximately 0.31 eV above S_1.

4. In the medium-pressure gaseous benzene system, Poole (100) has found that the $S_1 \rightarrow S_0$ fluorescence yield drops to zero for excitation of wavelengths of 240 nm or less, despite efficient collisional deactivation.

Such triplet yields, as are available, show that the vibrationally enhanced process is not intersystem crossing.

All of these observations are consistent with the existence of a rapid nonradiative route available for the decay of excited benzene molecules with energy approximately 0.30 eV above S_1. The variation with temperature of the quantum deficit $\emptyset_{IC} = 1-(\emptyset_F+\emptyset_T)$ has been analyzed kinetically in terms of a single process for benzene-h_6 (91,147) and benzene-d_6 (127) in solution. The assumption of a single decay process allows interpretation of the behavior with temperature of the rate constant k_{ICM} (= $\emptyset_{IC}/\tau_F$) in terms of the Arrhenius equation which yields an activation energy which is solvent dependent (91), typically of the order of 0.25 to 0.37 eV, and is tentatively interpreted as the mean excess energy required by the thermally equilibrated excited benzene molecules, for decay via this hidden route.

There is also evidence (105) that the quantum deficit increases with temperature in the high-medium-pressure gaseous system. Analysis using the crude model applied to the solution phase data produces an "activation energy" for Channel III decay of 0.14 eV for C_6H_6 and 0.19 eV for C_6D_6. A kinetic scheme involving a nonquenchable radiationless decay of vibrationally excited S_1 states is thought (105) to provide a better fit for the data. Using this approach, the onset of nonradiative deactivation would occur at approximately 0.4 eV above S_1.

The experimental evidence proves, without question, the existence of a Channel III route; and various attempts have been made

to provide some explanation. The theories of radiationless
transitions applied with varying success to the $T_1 \rightarrow S_0$ step
(see section X) have not yet been able to explain satisfactorily
the pure singlet decay phenomenon. It has been suggested that
photochemical rearrangements could account for the quantum de-
ficit. Evidence (184) (reviewed later in Section XII) has shown
that the prismane and Dewar isomers would arise from states of
B_{1u} symmetry, while benzvalene and fulvene result from the $^1B_{2u}$
state. Bryce-Smith and Longuet-Higgins (65,185) and Jano (186) have
suggested that diradical intermediates consistent with the sym-
metries of the $^1B_{2u}$ and $^3B_{1u}$ states may be involved in the photo-
isomerization of benzene and its derivatives. Measured radical
yields are very low (180), as are the final yields of isomeric
products (187). Though rapid re-aromatization of the diradical,
or of benzvalene has been proposed as an explanation of the low
isomer yields, it is to be expected that isomerization due to
group shifts should occur in the case of benzene derivatives.
Examination of the photodecay processes in o-xylene (188) and
m-xylene (189) has shown that aromatic isomer products are formed
in very small yields, and further, that the activation energy
for production of m-xylene from other isomers (0.44 eV) is higher
than the activation energy required for the temperature-dependent
Channel III process (0.21 eV). Birks (190), adopting the isomer
theory of Lamola et al. (191) and Noyes and co-workers (192),
suggests a "physical" isomer, the most unusual property of which
seems to be that, by definition, it is undetectable. It is sug-
gested that the potential energy surfaces of this "isomer" over-
lap with those of S_0 and S_1 benzene, permitting rapid hidden de-
cay. It is not clear how this differs from what would be con-
ventionally regarded as internal conversion.

    Callomon, Leach, and Lopez-Delgado (27) suggested that a
$\sigma-\pi^*$ state existed in the region between the $^1B_{2u}$ and $^1B_{1u}$ states
(see Section II), and selected $^3E_{2u}$ as the most probable state
involved. It has been suggested (156) that a singlet state would
be more plausible in view of the very high rate constant for the
transition from the $^1B_{2u}$ state. The problem of decay of this
newly invoked state remains since it is expected that the transi-
tion to ground state would be extremely forbidden, leading con-
sequently to a long-lived intermediate. Recent photochemical
data (193,194) have shown the existence of a long-lived, non-
benzvalene (194) intermediate following 2537 A^o irradiation of
benzene. Results obtained by Stein (94,195) in O_2-free solu-
tions of benzene have indicated the formation of benzvalene with
an initial quantum yield of 0.18 after excitation with the
2537 A^o line and that this initial yield is independent of temper-
ature in the 9 to 50°C range. This result shows that isomer

formation does not account for the thermally activated fluores-
cence quenching. Stein proposed that benzvalene arises from a
higher vibronic state before vibrational relaxation to the S_1
fluorescent state, that is, prior to interaction with the en-
vironment. Benzvalene is subsequently quenched by benzene trip-
let. Results of Lutz and Stein (195) also show an increase in
the efficiency of benzvalene formation at higher temperatures,
consistent with a decrease of $\emptyset_T$, as determined by Cundall and
co-workers (196). Further results of Ilan and Stein (197) on
the fluorescence yields of benzene solutions in the presence of
xenon still support the assumption.

   A recent tunneling effect model for radiationless transitions
(198) has been applied to benzene and other aromatic hydrocarbons.
The CH stretching vibrations are considered as dominant for the
non-radiative process. Rate constants for the radiationless pro-
cess $S_1 \rightarrow S_0$ calculated by theory are of the same order of magni-
tude as those obtained by experiment. A further possibility for
the interpretation of Channel III is a delay via a configuration-
ally perturbed doubly excited E_{2g} state, though this route seems
unlikely following confirmation that the relevant state is of
similar energy to $^1B_{1u}$ (see Section II).

IX.   THE $T_1 \rightarrow S_0$ PHOSPHORESCENCE TRANSITION

   Considering the ease with which phosphorescence emission
from solid or glassy phase solutions of benzene is observed,
it is perhaps surprising that unambiguous data on the probabil-
ities of radiative and radiationless decay of the triplet state
are so difficult to obtain and unreliable. The determination
of excited state parameters at a particular temperature requires,
at least, evaluation of $\emptyset_P$, $\emptyset_T$ and τ_P, and more reliably $\emptyset_P$, $\emptyset_F$,
$\emptyset_T$, τ_F, and τ_P. Direct measurement of $\emptyset_P$ by comparison of the
emission of the given compound with that of a standard sample is
one method of approach (148,150). However, since it is neces-
sary that both sample and standard possess identical optical
properties (otherwise corrections for effects of refractive index
differences, reflectivity losses, and emission polarization on
the measurements must be made), this method is of limited ap-
plicability. Other methods for measuring $\emptyset_P$ have been reported.
Kellogg and Bennett (199) estimated phosphorescence yield from
measurements of acceptor molecule fluorescence, resulting from
triplet energy transfer from the aromatic donor molecule. This
method should be reliable, provided solutions are sufficiently
dilute to eliminate the effect of triplet-triplet annihilation
and provided corrections for anisotropy of emission are made.

A further method involves a comparison of the luminescence from
a glassy sample with the light scattered by a MgO surface (149).
Because of the complexity and difficulty in obtaining re-
liable data, some authors (8,200,201) have made the arbitrary as-
sumption that $k_P = 0.030$ s^{-1} and is independent of temperature
for all unsubstituted hydrocarbons. From this assumption, and
measurements of τ_P, values for k_{GT} have been estimated. The
subsequent theoretical analysis of the radiationless transition
probability based on the assumption must, therefore, be treated
with some caution, since it is arbitrary and probably incorrect.
A method for determining k_P reported by Cundall and Pereira
(91) utilizes data from the parallel studies on parameters con-
trolling the spin-allowed emission. In these studies, most ex-
haustively pursued for benzene, it is found that both k_F and
k_{ISC} approach limiting low-temperature values, and estimates
of their magnitude in the < 100°K region may be given with some
certainty. With this information, the additional data for τ_P
and for ϕ_P/ϕ_F (χ), k_P can be determined, since

$$k_P = \chi \; k_F \; / \; k_{ISC} \; \tau_F$$

This method does not rely upon any special assumptions, although
corrections for photoselection effects (202-205) and for the
eigenpolarization of the spectrophotometer must be undertaken.
Further studies of fluorescence and phosphorescence at 77°K
for simple benzene derivatives using the same spectrophotometer
and the same optical arrangement carried out by Cundall and
Ogilvie (158) have shown that photoselection and eigenpolari-
zation corrections do not alter the results obtained for k_P
(within 2-3%). The above method assumes reliable data for τ_P
but measurements are subject to uncertainty. Variations in
τ_P for a specific sample can be found which depend upon the rates
of cooling of the sample, and also upon the time which elapses
between the freezing process and the measurement operation. The
cooling rate may affect the decay if two phases of the solid sol-
vent can be formed (206-208). This is the case for cyclohexane
matrices in which cubic matrices are produced by rapid freezing,
and monoclinic matrices by slow freezing. Variations in τ_P with
standing time can be observed if glass relaxation occurs (208-
210) and/or thermal equilibration is achieved only slowly (211).
Though the effect of this latter factor may be reduced by using
very narrow sample tubes, Martin and Kalantar (212) have shown
that τ_P varies considerably with time elapsed following freezing,
if the solvent utilized undergoes glass transitions in the neigh-
borhood of the temperature used. For the particular case of
benzene, τ_P is strongly dependent upon solvent and upon tempera-
ture above 60°K. Solvent effects have been reported by

Leubner (213), Hirayama (214), and Hatch et al. (215), among others (Fig. 8). In some instances, apparent solvent effects may be the result of impurity quenching, particularly in solvents of relatively low viscosity. However, this explanation cannot be universally valid and does not assist in understanding the unexpected temperature effect. Leubner (213) could find no correlation between sample viscosity and τ_P, and Ling and Willard (216) reported, from measurements on 3-methyl pentane between 77 and 94°K, that the viscosity had a pseudo-activation energy of 15.9 kcal/mol, a factor of 7 greater than the activation energy measured in much the same temperature range for τ_P. A definitive examination of the problem has been published recently by Kilmer and Spangler (217)(Fig. 9). These authors found that the variation in τ_P for benzene in cyclohexane ($\sim 10^{-3}$M) with temperature could be fitted to the relationship of the type

$$1|\tau_P = 1|\tau_o + k_1 \exp(-\Delta E|KT)$$

For benzene-h_6 it was found that $\tau_o = 11.44s$ $\Delta E/hc = 554$ cm^{-1} and $k_1 = 4.2 \times 10^3 s^{-1}$. The values for C_6D_6 are 14.28s, 705 cm^{-1} and $218 \times 10^3 s^{-1}$, τ_P is, of course, a composite function including radiative and nonradiative decay processes and there is still speculation concerning which mode of decay is temperature dependent and which not. The weight of evidence seems to favor the nonradiative route as being that which requires thermal activation. Use of the Kilmer-Spangler equation to extrapolate to room temperature produces phosphorescence lifetimes of 3.8 and 5 ms for C_6H_6 and C_6D_6, respectively. Since phosphorescence is not observed in either liquid or gas phases, it is clear that alternative decay routes operate in fluid media.

Some emission lifetime data are presented in Table 14. Particularly of note are the lifetimes in frozen inert gas solutions, reflecting the enhancement of $T_1 \rightarrow S_0$ transition with increasing atomic number of the solvent; an effect also noted by other authors. The important results of Haaland and Nieman (222) show a marked solvent effect on phosphorescence lifetimes. Perfluorocarbons are the least perturbing solvents on phosphorescence, an effect consistent with results obtained in liquid solution (72,91).

The effect of deuteration whose influence is independent of solvent and temperature, shows the importance of the importance of the C-H/C-D modes in promoting one or both of the triplet decay transitions.

Using the values $\phi_F = 0.2^{120}$, $\chi(=\phi_P/\phi_F) = 0.92$ (92,219) and $\tau_P = 5.50$ s for benzene in methyl cyclohexane, it is possible to calculate values of 0.0417 and 0.401 s^{-1} for k_P and k_{GT}. The

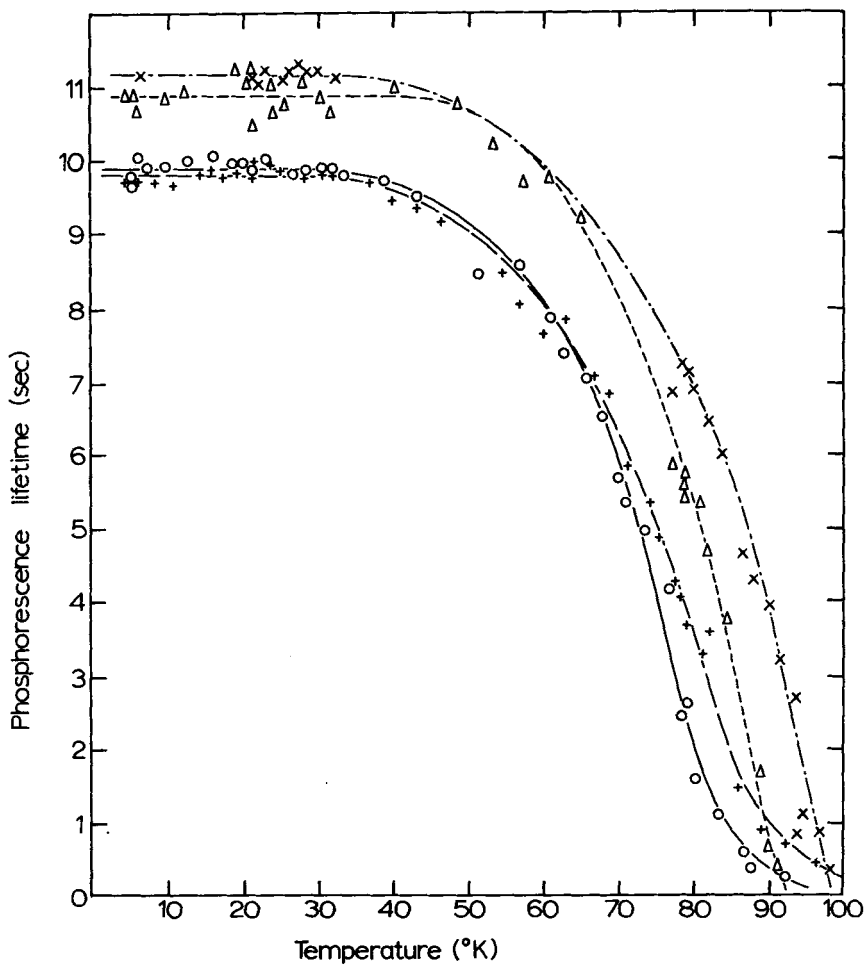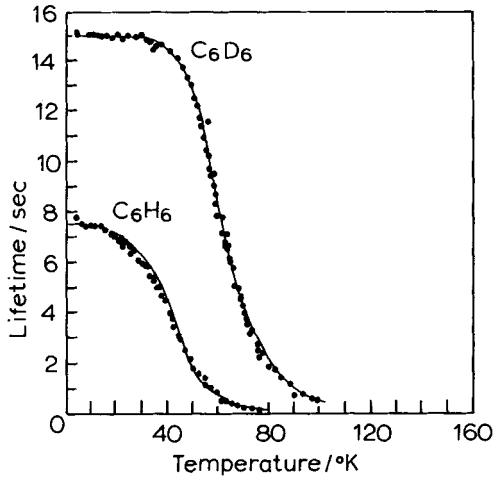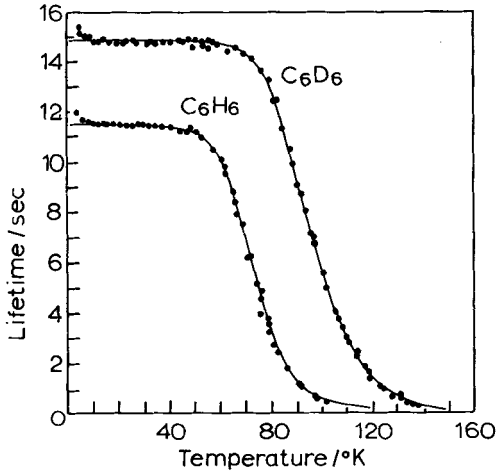FIGURE 8. Temperature dependence of τ_p for C_6H_6 in ethanol (X), EPA (Δ), 3-methylpentane (0), and MCH-isopentane (+), (Leubner).[213]

(b)

(a)

FIGURE 9. Temperature dependence of τ_p for C_6H_6 and C_6D_6 in (a) cyclohexane and (b) cyclopentane, (Kilmer and Spangler).[217]

TABLE 14.   Phosphorescence lifetimes for dilute benzene solutions.

τ_p (s)	Isomer	Solvent	Temp. ($^{\circ}K$)	Remarks	Ref.
7.1	C_6H_6	EOA	77		(144)
17.5	C_6H_6	–	20	Two sites for decay	(171)
29.5	C_6D_6	–	20	This for longest	(171)
5.75	C_6H_6	3-Methylpentane	77	Relaxed	(218)
7.48	C_6H_6	Isopropanol	77	Frozen quickly	(218)
4.75	C_6H_6	Cyclohexane	77	Monoclinic	(218)
12.02	C_6D_6	3MP	77	Relaxed	(218)
13.69	C_6D_6	Isopropanol	77	Frozen quickly	(218)
14.10	C_6D_6	Cyclohexane	77	Monoclinic	(218)
5.50	C_6H_6	Methyl-cyclo-hexane	77	Frozen quickly	(219)
6.50	C_6H_6	Ethanol	77	Frozen quickly	(92)
5.50	C_6H_6	Methanol	77	Frozen quickly	(92)
10.50	C_6D_6	Methyl-cyclo-hexane	77	Frozen quickly	(219)
11.20	C_6D_6	Ethanol	77	Frozen quickly	(92)
9.10	C_6D_6	Methanol	77	Frozen quickly	(92)
9.83	C_6H_6	Me-cx/IP	<60	Independent of	(213)
9.92	C_6H_6	3-Methylpen-tane	<60	temperature below	(213)
10.91	C_6H_6	EPA	<60	$60^{\circ}K$ but	(213)
11.19	C_6H_6	Ethanol	<60	solvent dependent	(213)
9.0	C_6H_6	Dioxane	77	–	(214)

TABLE 14 (cont.)

5.90	C_6H_6	EPA	77	–	(214)
2.0	C_6H_6	Cyclohexane	77	–	(214)
5.78	C_6D_6	Isopentane	77		(212)
11.79	C_6D_6	3-Methylpentane	77		(212)
12.11	C_6D_6	3-Methylhexane	77		(212)
11.31	C_6D_6	Methyl-cyclo-hexane	77	Constant	(212)
13.70	C_6D_6	Ethanol	77	values after	(212)
13.40	C_6D_6	Iso-propanol	77	solvent	(212)
13.06	C_6D_6	EPA	77	relaxation	(212)
9.46	C_6D_6	Cyclohexane	77		(212)
10.32	C_6D_6	Isooctane	77		(212)
5.75	C_6H_6	3-Methylpentane	77		(212)
8.45	C_6H_6	EPA	77		(212)
3.04	C_6H_6	3-Methylpentane iso-pentane	77		(212)
11.44	C_6H_6	Cyclohexane	–	Limiting	(217)
14.82	C_6D_6	Cyclohexane	–	low-temperature	(217)
7.46	C_6H_6	Cyclopentane	–	values	(217)
14.94	C_6D_6	Cyclopentane	–		(217)
29.5	C_6D_6	Argon	20		(171,220)
14.5	C_6D_6	Argon	20		(171,220)
17.5	C_6H_6	Argon	20		(221)
0.74	C_6H	Krypton	20		(221)

TABLE 14 (cont.)

0.026	C_6H_6	Xenon	20		(221)
29.5	C_6D_6	Argon	20		(221)
0.025	C_6D_6	Xenon	20		(221)
15.4	C_6H_6	Perfluoromethyl-cyclohexane	65		(222)
10.9	C_6H_6	Methyl-cyclo-hexane	65		(222)
23.7	C_6D_6	Perfluoro-cyclo-hexane	65		(222)
14.3	C_6D_6	Methyl-cyclo-hexane	65		(222)
8.0	C_6H_6	EPA	77		(148)
11.8	C_6H_6	Cyclohexane	4.2		(215)
10.2	C_6H_6	Borazine	4.2		(215)
9.5	C_6H_6	C_6D_6	4.2		(215)
15.6	C_6D_6	Cyclohexane	4.2		(215)
12.5	C_6D_6	Borazine	4.2		(215)
6.3	C_6H_6	EPA	77		(154)
9.4	C_6D_6	EPA	77		(154)
4.6	C_6H_6	EPA	77	Monoclinic	(207)

phosphorescence rate constant for benzene is in close agreement
with that of Johnson and Ziegler (171) who deduced a value of
0.041 s^{-1} for C_6H_6 and 0.034 s^{-1} for C_6D_6. The latter authors
concluded that deuteration affected the vibronic coupling neces-
sary to promote the radiative transition and that the deuter-
ation effect on the radiationless transition is small at variance
with early theories of radiationless transitions (201,223).
    From the variations of τ_P with temperature, Kilmer and
Spangler (217) concluded that the ratio k_P k_{ISC}/k_F was independent

of temperature and equal to 0.229 ± 0.007 s. Although both
k_F (134) and k_{ISC} (147) may increase with temperature above
ambient, by analogy with toluene (156) and other methylated
derivatives (224) it is expected that both will be nearly con-
stant below room temperature. From a combination of these data
it is clear that k_p is independent of temperature.

All of the above data refer to dilute solutions; the effect
of solute concentration on the phosphorescence emission yield
and lifetime is very marked. At concentrations of 1M and above,
a decrease in τ_p and the χ ratio has been reported for EPA (214),
EOA (144,152), methylcyclohexane (219), and cyclohexane (207).
Phosphorescence is negligible in both pure benzene crystals (225)
and polycrystalline powder (144,214). This has been attributed
to a rapid triplet-triplet annihilation process, an explanation
apparently confirmed by Cundall and Pereira (219), who detected
solution some slight rather diffuse phosphorescence together with
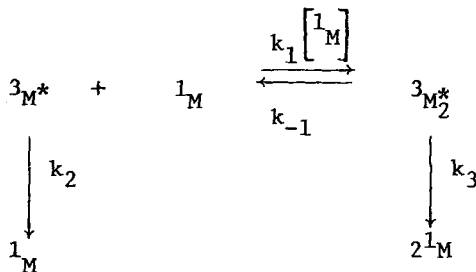delayed fluorescence from pure benzene.

X. THE $T_1 \rightarrow S_0$ RADIATIONLESS TRANSITION

The benzene triplet has not been observed to phosphoresce
in either the gas or liquid phase, as noted previously but in
view of the lifetime measured in glassy media at low temperature
this is not surprising, since very small amounts of quenching
impurities would reduce emission to undetectable levels. Some
detailed investigations have shown that there is an intramolecular
process which induces radiationless decay of the benzene triplet
state, other than impurity quenching.

By competitive methods Ishikawa and Noyes (226) (sensitized
biacetyl phosphorescence) and Cundall and Davies (159) (butene-2
isomerization) both estimated the triplet lifetime to be of the
order of 10 μs. In a reexamination of the butene-2 system, Lee
(227) estimated a value of 100 μs, a finding confirmed by Cundall
and Dunnicliff (105). An examination of the kinetics of the
benzene photosensitized composition of cyclopentanone decomposi-
tion allowed a value of longer than 3 μs to be deduced. This
type of experiment is far from satisfactory since photochemical
processes can intervene at low pressures, and impurities and the
quenching effects of photoproducts can affect the results. These
problems can only be overcome by some form of direct measurement.
Parmenter and Ring (228) used a flash method in which 20 torrs
of benzene and 0.01 torr of biacetyl were submitted to a 20 J,
3 μs flash of 250 to 260 nm light. From the time dependence of
the biacetyl phosphorescence emission, a lifetime of 26 ± 5 μs
was deduced. Lee (227) cites a private communication from
Parmenter in which the lifetime of the gaseous triplet is given

to be 70 ± 20 μs for 2 torrs benzene. Burton and Hunziker (229) have developed a modulated transient absorption technique that uses Hg 6^3P_0 atoms to populate the benzene triplet state. The decay of the triplet is observed by an absorption band at 231.5 nm, assigned to the allowed $^3E_{2g} \rightarrow {}^3B_{1u}$ absorption (36), with f-values of 0.07 and 0.06 for light and heavy benzene, respectively. The decay is pseudo-first-order, resulting from bimolecular triplet-triplet interaction. The results are viewed guardedly by other workers because of effects that may arise from the high light absorption which must be used. First order decay rates of $3 \times 10^3 s^{-1}$ and $2 \times 10^3 s^{-1}$ were calculated for the presence of 300 to 800 torrs of nitrogen, needed to promote the Hg $6^3P_1 \rightarrow 6^3P_0$ transition. The pulse radiolysis of naphthalene/benzene vapor mixtures at 390°K has given data which can be used to calculate $1.3 \times 10^5 s^{-1}$ for the decay constant of the $^3B_{1u}$ state of benzene at a partial pressure of 18 torr (230), from the naphthalene triplet absorption following irradiation.

A new experimental approach to the problem has been used by Hunter and Stock (231) involving measurement of the frequency dependence of the acoustic signal resulting from transformation of electronic excitation from vibrational to translational energy, consequent to excitation of the $^1B_{2u}$ state. This technique was used to measure the decay of the benzene triplet over the range 0 to 6 torrs, and it was found, in agreement with what could be inferred from some of the earlier work, that decay of the triplet depends upon benzene concentration. The pressure-independent decay process was found to have a rate constant of $(1.7 \pm 0.1) \times 10^3$ s^{-1} and a collision efficiency of 1.6×10^{-4} deduced for the second order self-quenching process. The authors claim to have discounted the effects of deactivation by traces of oxygen. A strong perturbation of the $^3B_{1u}$ state by ground state $^1A_{1g}$ molecules seems the most likely mechanism for accounting for the observed concentration dependence; and involvement of the triplet excimer is in accord with the following scheme.

$$^3M^* \quad + \quad {}^1M \quad \underset{k_{-1}}{\overset{k_1[^1M]}{\rightleftarrows}} \quad {}^3M_2^*$$

$$\downarrow k_2 \qquad\qquad\qquad\qquad\qquad \downarrow k_3$$

$$^1M \qquad\qquad\qquad\qquad 2\,{}^1M$$

The reciprocal of the triplet lifetime $\tau_T{}^{-1} = k_2 + k_3(k_{-1}+k_3)^{-1}$ $k_1[^1M]$. Analysis of the results shows the $k_3(k_{-1} + k_3)^{-1}$ is 1.6×10^{-4} and thus $k_{-1} \gg k_3$. This contrasts with the situation in other aromatic hydrocarbons in solution where triplet-ground state interaction is proposed to explain similar shortening of measured triplet lifetime (232); in these cases, it would seem that $k_3 \gg k_{-1}$.

The self-quenching mechanism which has been invoked for the gas phase system applies also to the liquid phase. Order of magnitude agreement between data from the various techniques for measuring τ_T seems to have been achieved. Cundall and Griffiths (233), obtained the first indications from studies on the benzene/butene-2 system, that the triplet state lifetime was very short. The value for $k_{ET} \tau_T$ was 21.2M at 25°C where k_{ET} was the overall rate constant for triplet excitation energy transfer from benzene to butene-2, and τ_T the lifetime of the benzene triplet. Assuming a value of about 5×10^9 $M^{-1}s^{-1}$ for k_{ET}, τ_T appears of the order of a few nanoseconds. Although the kinetic analysis may have oversimplified (175), the order of magnitude lifetime is similar to that determined from the work of Kaufman (234) and Hentz and Perkey (176) and also consistent with the results of Dubois (235,236) who failed to detect any evidence for triplet energy transfer to biacetyl in pure benzene. By contrast, Lipsky (237), Sandros (181), and Russian workers (238,239) observed triplet energy transfer from benzene to biacetyl for dilute benzene solutions. This indicates that the triplet lifetime in solution is also concentration dependent as is the case for o-xylene (240) where the lifetime increased from a few nanoseconds to microseconds or more, on dilution. This has been confirmed for benzene (175,189) and further, additional evidence from photochemical (173) and pulse radiolysis (241) systems demonstrate the very short lifetime of the triplet state in pure benzene liquid. It is believed (175) that decay proceeds via the triplet excimer which is only inefficiently quenched by butene-2. Results of electron impact excitation (242) and pulse radiolysis (243) have indicated a triplet lifetime of 500 µs for gaseous benzene at low and high pressures.

Attempts to directly detect the triplet state of benzene under these or similar conditions by transient spectroscopy techniques have so far been unsuccessful. Thomas and Mani (244) found a transitory species with an absorption maximum and a decay time of 112 ns in benzene and benzene cyclohexane mixtures. The results from addition of naphthalene, biacetyl, oxygen, and piperylene suggest that this is a product of reaction between triplet and ground state benzenes. Build-in times for this species, which are 3 ns for pure benzene and 20 ns for 10 percent benzene/cyclohexane mixture are temperature independent. Laser

flash photolysis (179) results are consistent with a $T_1 + S_o$ reaction for triplet decay. This is the most that has been achieved to direct observation of the benzene triplet in solution at room temperature.

The lifetime of the triplet state of benzene in fluid solutions (at room temperature and above) is determined by the, seemingly efficient, interaction of that state with ground state molecules. This is not inconsistent with the low temperature behavior from which it has been deduced (51-55), that a thermally activated $T_1 \rightarrow S_o$ transition arises from distortion of the benzene ring which destroys the strict D_{6h} symmetry. Even below $65°K$, it is apparent that hydrocarbon solvents are not inert and that perfluorocarbons are the least perturbing of possible solvents (222). The concentration quenching mechanism must involve some, as yet unestablished, form of chemical or charge transfer interaction which reduces the forbidden character of the transition. There is no positive evidence to show that this process occurs at low temperature.

XI. TRANSITIONS FROM HIGHER (n > 1)EXCITED STATES

Several years ago, Braun, Kato, and Lipsky (142) showed that in the vapor solution and bulk liquids, benzene and its methylated derivatives appeared not to undergo efficient internal conversion or intersystem crossing from higher excited singlet states to form either S_1 or T_1 states. This was confirmed by Birks, Conte, and Walker (143) who postulated a scheme involving excimers of higher excited states, to explain their data and noted that benzene proved to be the exception amongst similar compounds in that the effect decreased on dilution.

Some more recent experimental evidence has been presented by Voltz and co-workers (145). Using 2-napthtyl-2-phenyl-5-oxazole-1.3 an excitation energy acceptor, these authors obtained results similar to those of Lipsky (142), but also found that autoionization occurred at wavelengths below 175 nm. There is low efficiency of conversion of B_{1u} and $^1E_{1u}$ to the $^1B_{1u}$ state, and relative efficiencies of fluorescence are constant but different over each of the main bands. Voltz (145) also claims that energy transfer occurs from S_2 and S_3 states, in agreement with Laor and Weinreb (245) but at variance with Lawson, Hirayama, and Lipsky (72,246). Electron scavengers such as O_2 and $CHCl_3$ which affect the S_3 and S_2 states to only a negligible extent, influences the ionization effects at higher excitation energies.

Lawson, Hirayama, and Lipsky (72,246) also measured the variation in quantum efficiencies for internal conversion from S_3 to S_1 in several solvents and found that the values vary very markedly. The efficiencies measured were 0.45 in pure benzene, 0.37 to 0.28 in alcohols and other polar solvents, 0.25 to 0.22 in aliphatic hydrocarbons, 0.04 in $n-C_6F_{14}$, and about zero in the gas phase. The order of effectiveness in a number of solvents paralleled the enhancement of the 0-0 band in absorption. The implication would seem to be that solvent perturbation produces state mixing and consequent enhancement of internal conversion $S_n \rightarrow S_1$.

Other types of experiment give information about the internal conversion processes of higher excited singlet states. Lumb, Braga, and Pereira (144) measured the fluorescence and phosphorescence excitation spectra of rigid solutions of benzene in ether/isooctane/alcohol glasses at $77^\circ K$. The two excitation spectra were identical, showing that $\emptyset_F$ and $\emptyset_P$ vary in the same manner with λ_{ex}. The efficiencies of conversion from higher levels are not zero, but depend upon concentration; a surface quenching mechanism may be involved.

Direct observation of fluorescence from higher singlet states of benzene and some methyl derivatives has recently been achieved by Hirayama, Gregory, and Lipsky (247). Using apparatus capable of detecting fluorescence yields as low as 10^{-6} they recorded the emission spectra from oxygenated solutions of pure benzene and other aromatics excited at 184.9 nm. Subtraction of the tail of the residual S_1 emission gives a fluorescence spectrum with λ_{max} approximately 235 nm and $\emptyset_F = 8 \times 10^{-6}$ for benzene. This is assigned to an S_2-S_0 emission.

In 0.1M solutions of p-xylene and mesitylene, emissions could also be detected for the S_3-S_0 transition. Similar successes have also been achieved with p-xylene, toluene, and mesitylene, in the vapor phase, leading to the hope that data for benzene vapor may soon be forthcoming.

Some information is available on the photochemical effects that occur after the formation of higher excited states, which may help, in part at least, to explain some of the effects. Foote, Mallon, and Pitts (248), and Shindo and Lipsky (249) investigated the photochemistry of benzene vapor, excited into the S_3 state. Both sets of data, when extrapolated to zero pressure, give a quantum yield of unity for chemical reaction. The isomer formed was later (250) shown to be fulvene, with some polymer formation. This route for energy decay will be examined in the following section.

## XII. RELEVANT PHOTOCHEMICAL REACTIONS OF
EXCITED STATES OF BENZENE

As previously stated, molecular isomerization does not pro-
vide an explanation for the quantum deficit following excitation
of benzene; the first band does not bear close scrutiny. How-
ever, an investigation of the photochemistry of excited benzene
is of interest, in view of the variety and complexity of the iso-
meric products. An extensive review of conditions under which
the formation of isomers of benzene and its derivatives can be
found has been compiled by Scott and Jones (250). Interconver-
sion of the isomers which would be relevant to photophysical ef-
fects are governed by orbital symmetry considerations, and exam-
ples of this type of treatment are now appearing (251,252).

In 1966, Bryce-Smith and Longuet-Higgins (65,185) suggested
a scheme that seems to provide a generally satisfactory descrip-
tion of the facts. Prefulvene and Dewar-like intermediates con-
sistent (184) with the symmetry of the $^1B_{2u}$, and $^3B_{1u}$ excited
states which supposedly give rise to them, have been proposed.
The existence of these intermediates has not been proven, and for
heavily substituted fluoro-benzenes, Dewar isomeric forms arise
from excited singlet states in apparent contravention of the sym-
metry considerations (253,254). The significance of this is not
clear.

No attempt is made here to review all the experimental
data, but some investigation relevant to the theme of this
article will be cited. Wilzbach, Kaplan, and Harkness (255)
showed that benzene-1,3,5,d_3 rearranged to the 1,2,4-isomer when
excited at 254 nm in the vapor phase, and deduced that this oc-
curred through a benzvalene intermediate with a yield of about
3 percent. Subsequently, Kaplan and Wilzbach (256) isolated
benzvalene, from benzene excited within the first band, with a
yield of 0.02. Addition of added gases increases the yield by
stabilization of "hot" benzvalene molecules. The data on the
effect of exciting wavelength shows that relaxation from higher
vibrational levels of the S_1 state is accompanied by a decrease
in the yields of both fluorescence and triplet production. The
work of Kaplan and Wilzbach provides some evidence for an in-
crease in the yield of benzvalene in going from 254 to 237 nm,
but no correlation with the sharp increase in nonradiative decay
when the vibrational energy exceeds 2500 cm^{-1} has been achieved.
An interesting argument against benzvalene formation providing
a complete explanation of the nonradiative processes has been
advanced by Spears and Rice (111). The conservation of angular
momentum must inhibit conversion of benzene into benzvalene, but
no correlation of rotational energies with either radiative or

nonradiative rate constants was found by Parmenter and Schuh
(257). As pointed out in Section VIII, recent results of Stein
(195) have indicated that isomerization cannot explain completely
Channel III in benzene.

More work on the photochemistry of benzene cannot fail to be
informative. A recent example of the type of experiment that
shows promise is that reported by Irina and Kurien (194). Phenol
and mucondialdehyde are major products found from the photolysis
of benzene vapor in the presence of oxygen, and also that phenol
alone is formed in the absence of oxygen on interaction with
water. The experimental conditions employed a flow of the vapor
through a trap, indicating that the products formed must have
resulted from the interaction of a long-lived excited inter-
mediate with water. This intermediate cannot be benzvalene since
it has been established (258) that this reacts with water to give
a cyclo pentadiene-1-carboaldehyde, via the following mechanism:
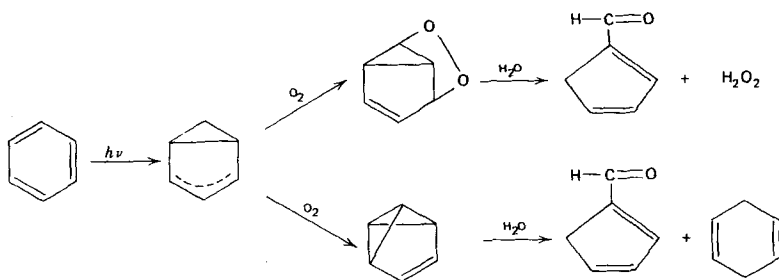
"Internal conversion" in the liquid and solid phases is still
obscure. Decomposition and isomerization yields are small,
usually of the order of 0.01, and in general are very much less
than in the gas phase, presumably due to the rapid collisional
stabilization that can occur in condensed phases.   Formation
of an intermediate of the pre-fulvene type would require several
quanta of ring-deforming vibrations, and this could account for
the decrease in yields with lowering of temperature.

Since the efficiency of "internal conversion" is greater in
solution than in the gas phase, and since the controlling para-
meters are, to a certain extent, solvent dependent (91,94), the
possibility of chemical reactions with solvent by excited state
routes cannot be ignored. Experimental difficulties have pre-
vented very clear results. This is illustrated by the discordant

data on the reaction of oxygen with benzene under various condi-
tions (130,259-261).

It has been known for some time that hexatrienes can be
formed by reaction of excited benzene molecules with solvent
in a frozen glass (262-264). Some details of the mechanism of
this process have been deduced by Simons and Smith (90). They
propose that intermolecular vibronic interaction with solvent is
a necessary but not sufficient requirement for production of
hexatrienes in viscous media. The reaction is associated with
radiationless decay of the triplet state rather than a bimole-
cular reaction of triplet benzene with neighboring solvent
molecules. Since radiationless decay constitutes intersystem
crossing, the product of the reaction is also in the ground state.
It is stressed by the authors that hexatrienes are not produced
in fluid media or by nonphosphorescent benzene derivatives in
which there is a rapid competing decay of the triplet state.
The formation of the hexatriene only occurs when weak interactions
occur between the relaxing triplet and the solvent.

Assignment of nonradiative decay from the S_1 state of ben-
zene to both internal conversion and triplet formation by inter-
system crossing requires that the triplet yield measurement tech-
niques used should be reliable and that chemical reactions of
excited states with triplet monitoring reagents do not occur.
As a rule, in the case of olefins, which have been most used as
triplet scavengers for benzene, it is reassuring to find that for
the types of olefin used as triplet monitors addition products
are usually only formed in very small yields (265,268). Consis-
tency with triplet yields obtained by other methods give some
further confidence that the technique used, in general, provide
self-consistent results.

Examples of the type of agreement are given for the gas
phase in the recent review of Noyes and Al-Ani (269) and compari-
son of triplet yields in solution obtained by Sandros (146,181)
using biacetyl as the scavenger, and Cundall et al. (147,156,157)
using butene-2.

XIII. BENZENE EXCIMER

The formation of a benzene dimer from association of a
ground state monomer and an excited monomer is a well-established
observation of this species was first noted by Dammers de Klerk
(270) and Ivanova and co-workers (271) in a study of the effects
of concentration on the fluorescence spectrum of benzene. Broad
structureless emission on the long wavelength side of monomer
emission at room temperature is clearly observed at concentrations

of about 1M, and a further increasing concentration becomes the
dominant component in the spectrum.

The existence of such a dimeric species, stable in the ex-
cited state, and experiencing dissociative repulsive interaction
in the ground state, is explained (272) in terms of configura-
tional interaction between excitation and charge resonance states
of the dimer. Its structure is generally believed to be of an
eclipsed parallel plate form, though Birks and co-workers (273-
275) favor a slightly displaced structure with one molecule over-
lapping the other. The study of Birks and Christophorou (276)
has shown that the net excimer binding energy is dependent upon
intermolecular separation, and it seems well established that the
particular ring separation in benzene is 0.31-0.33 nm.

The excimer so described is singlet in character, and many
authors (272,277,279) have suggested that emission to the repul-
sive ground state is dipole forbidden. It is possible (272) that
a small rotation from the strict parallel plate configuration
is sufficient to remove this restriction, and Chesnut et al.
(280) have shown that a rotation of 30 degrees decreases the
excimer binding energy by 0.01 eV. This would suggest that
excimer emission probability may be temperature dependent; and
such has been found to be the case by Hirayama and Lipsky (125,
281) and Cundall and Robinson (134), but not by Birks and co-
workers (282).

The parameters that describe the properties of the excimer
state may be extracted from kinetic analysis of transient and
steady state luminescence data. The scheme due to Birks,
Braga, and Lumb (131,274), although criticized for its simpli-
city (125,283), accounts well for experimental decay of the
singlet excimer. The observed quantum yield of monomer fluores-
cence $\emptyset_{FM}$ is reduced in the presence of excimer from the intrin-
sic yield $\emptyset_{FM}^{o}$ according to:

$$\emptyset_{FM} = \emptyset_{FM}^{o} c (1 + c | c_h)$$

where $1 | c_h$ is the Stern Volmer quenching parameter such that
$\emptyset_{FM}$ at $c = c_h$. A similar expression for excimer fluorescence
is

$$\emptyset_{FD} = \emptyset_{FD}^{o} (1 + c_h | c)$$

Two evaluations of c_h are thus possible for all temperatures
where excimer band emission can be observed. Cundall and
Robinson (134) showed that the temperature of c_h led to the de-
duction that $(E_b + E_{ICM} - E_{ICSD}) = 0.38$ eV. (here subscripts
refer to processes described in the introductory section).
Excimer fluorescence lifetimes, τ_D can be extracted from know-
ledge of the measured emission lifetime of more concentrated

solutions, and the intrinsic monomer lifetime τ_M, according to:

$$\tau_{obs} = \frac{\tau_M + \tau_D(c/c_h)}{1 + c/c_h}$$

Combination of this data with that of the intrinsic excimer emission yield $\emptyset_{FD}^o$ allows computation of k_{FD}, the excimer fluorescence probability. Cundall and Robinson (134) found that the rate constant so calculated had an associated activation energy of 0.15 eV, assigned to thermal distortion of the dimer to overcome dipole restrictions on the emission. Helman (136,139) has found a concentration dependence for k_{FD}, and he speculates that this may be due to the formation of trimeric excited complexes.

Ludwig and Amata (135) also found it necessary to postulate the involvement of multimolecule complexes to explain some anomalies in the CCl_4 quenching of emission data. There is no direct evidence for such species, though they may exist, provided the exciplex is of lower potential than the singlet monomer molecule. The binding energy for such a species would be very small. This, together with the probable highly forbidden emission, might lead to difficulties in observation. Proof of the involvement of the types of species in the decay of the excimer remains unavailable.

The excimer binding energy deduced by Gregory and Helman (136) from transient luminescence decay data at low temperature (0.26 eV) is at variance with the conclusions of other authors (125,134) (≥ 0.36 eV) using steady state luminescence data. The problem lies in determining the temperature dependence, if any, of the ratio k_{FD}/k_{FM}, since all authors agree that the ratio k_{DM}/k_{MD} has a complete activation energy of approximately 0.25 (± 0.03) eV. Theoretical estimates of Vala, Hillier, Rice and Jortner (284) and Chestnut et al. (280) place the expected binding energy in the range 0.3 to 0.5 eV depending upon ring separation. The various parameters describing the singlet benzene excimer are summarized in Table 15, compiled with reference to Fig. 10.

The experimental difficulties involved in measurement of fluorescence yields and lifetimes for benzene, and other systems also, as a function of concentration make it certain that the various thermodynamic quantities have not yet been firmly established.

It is reasonable to presume that the routes for decay of the excimer are similar to those available for the excited monomer. There is no direct evidence for the existence of the triplet excimer although its existence has been invoked to explain anomalous triplet yield data (175). Hillier, Glass and
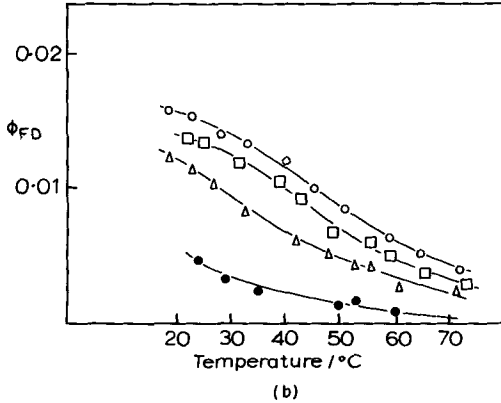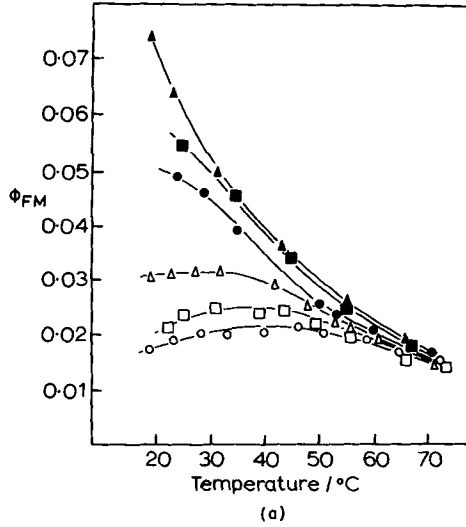
FIGURE 10. (a) Variation of monomer fluorescence
yield for benzene with concentration and temperature.
▲, 0.12 M; ▫, 0.51 M; ●, 1.12 M; △, 4.5 M; ▢, 7.9 M;
O, 11.2 M. (b) Variation of excimer fluorescence
yield with concentration and temperature. O, 11.2 M;
▫, 7.9 M; △, 4.5 M; ●, 1.12 M.

TABLE 15.   Decay parameters of the singlet excimer of benzene.

Parameter	Value	Temp. (°C)	Comments	Ref.
ϕ_{FD}^{o}	0.012	20	Hexane	(124)
	0.016	25	Methylcyclohexane	(125)
	0.022	20	Cyclohexane, T dependence	(134)
E_b	0.26	-30°C	Methyl-cyclohexane	(136)
	0.22	-	Cyclohexane	(282)
	≥ 0.36	-	Methyl-cyclohexane	(125)
	0.34	-	Cyclohexane	(134)
c_h	4.8	24	Hexane	(285)
	2.1	25	From monomer Me-cyclohexane	(125)
	5.0		From excimer	
	5.0	20	From monomer	
	16.1		From excimer cyclohexane	(283)
	5.0	25	From monomer	(134)
	4.65		From excimer (very T dependent)	
R_m	0.46 eV			(134)
	0.48 eV			(282)
ΔS^o	-29.6		(cal mol^{-1}K^{-1})	(134)
	-28		(cal mol^{-1}K^{-1})	(125)
	-20.3		(cal mol^{-1}K^{-1})	(282)
E_{FD}	0.145		(eV)	(134)
τ_D	12.3	25	From ionization studies	(286)
	12.	20	Hexane	(282)
	30	20	Cyclohexane	(134)

Rice (287) inferred its existence from elegant experiments in which they examined the phosphorescence emission of the para-cyclophane compounds. With the two benzene rings held together by methylene bridges in a sandwich structure, they observed shifted phosphorescence spectra with associated loss of structure; the most significant effects being at a ring separation of approximately 0.3 nm. Phillips and Schug (288) identified emission at about 4.30 nm in 1 MeV electron irradiated benzene at $138^{\circ}K$ with the triplet excimer.

Conclusive evidence of this elusive species awaits systematic studies using transient absorption techniques. Further, the characteristic excimer emission has not been observed in the solid phase, where intermolecular distances are such as to minimize the interaction and because achievement of the necessary orientation is inhibited in the frozen samples.

XIV. CONCLUSION

It is clear that the photophysical behavior of benzene is complex and that the nonradiative $S_1 \rightarrow S_0(?)$ process vaguely described at Channel III is especially important. It is not possible to conclude whether benzene is a "typical" aromatic molecule until comparably detailed studies of other systems have been made.

ACKNOWLEDGMENTS

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