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B_{2u} → A_{1g} Fluorescence Excitation Spectrum of Liquid Benzene from 250 to 150 nmVladimir O. Saik[†] and Sanford Lipsky*

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The B_{2u} → A_{1g} fluorescence quantum yield of benzene has been obtained for excitations from 250 to 150 nm in the solvents *n*-hexane, isooctane, *n*-perfluorohexane, *n*-pentane, cyclohexane, and *cis*-decalin. In *n*-hexane and isooctane, measurements have been made over a range of benzene concentrations from 0.112 to 11.2 M (the neat liquid). In dilute solutions, the sudden losses in fluorescence as the excitation wavelength sweeps from the first into the second absorption system and then again as the excitation wavelength sweeps from the second into the third absorption system are correlated with the behavior of benzene vapor in the region of channel three. Increasing the benzene concentration causes abatements in the rate of loss of fluorescence with decreasing excitation wavelength in the regions of the second and third absorption systems and, above 2 M, causes a reversal of this rate so as to cause a recovery of the fluorescence in the region of the third absorption system. These changes are correlated with the effects of benzene concentration on the electronic absorption spectrum and with reported effects of clustering on the multiphoton photoionization efficiency.

I. Introduction

Peculiar variations in the B_{2u} → A_{1g} (hereafter referred to as S₁ → S₀) fluorescence quantum yield of liquid benzene have been reported for excitations into upper electronic states S_n.¹ Since the S₁ → S₀ emission spectrum remains independent of excitation energy, these variations were interpreted to reflect changes in the efficiency with which upper states internally converted to the fluorescing state, S₁. The pertinent variable in these studies was the ratio β_f(λ) of the S₁ → S₀ fluorescence quantum yield Φ_f(λ) for excitation at wavelength λ to that at some wavelength λ₁ on the long-wavelength side of the S₀ → S₁ absorption system.

Thus, it was found that β_f(λ), although constant for any excitation wavelength within the first absorption system (i.e., equal to unity for λ₁ = 270–230 nm), declined rapidly on entrance into the second absorption system (beginning at ca. 225 nm) and continued to drop to a value of 0.5 at λ = 210 nm. From 210 to 200 nm, which spans the region of maximum absorptivity of the second absorption system,² A_{1g} → B_{1u} (S₀ → S₂), β_f(λ) remained relatively constant but then again plummeted on entrance into the third absorption system at λ = 200 nm and continued to decline to a value of 0.3 at λ = 190 nm. From 190 to 185 nm, an interval in which the liquid benzene A_{1g} → E_{1u} (S₀ → S₃) absorption exhibits a broad maximum,² β_f(λ) remained constant at 0.3. Below λ = 185 nm, as the S₀ → S₃ absorption spectrum begins to decline in absorptivity, β_f(λ) was observed to recover, achieving at λ = 150 nm the same value as at 210 nm of ca. 0.5 (and at 140 nm a value of 0.8).³

This peculiar anticoincidence of the spectrum of β_f(λ) vs λ (hereafter referred to as the fluorescence excitation spectrum) with the absorption spectrum was also obtained for neat liquid toluene, *p*-xylene, and mesitylene, albeit with somewhat less pronounced declines in β_f(λ) on entrance into the S₀ → S₂ and S₀ → S₃ absorption systems.^{1,3} Indeed, with increasing methyl substitution there appeared to be generally an approach of β_f(λ) to unity over the entire region of variation of λ from 270 to 120 nm.

A few measurements were also made on 4% by volume solutions of the aromatics in either cyclohexane or isooctane.^{1,3} Again, β_f(λ) remained unity within the S₀ → S₁ absorption system, declined sharply on entrance into the S₀ → S₂ system, and then again declined sharply on entrance into the S₀ → S₃ system. Measurements in these dilute solutions were only obtained to ca. 190 nm, and accordingly, no turnaround in β_f(λ) was observed. In the case of benzene, for all λ from 225 to 190 nm, β_f(λ) was significantly lower in the dilute solution than in the neat liquid. Several years later very similar results were reported by Birks et al.⁴

The addition of *p*-terphenyl to neat liquid benzene at a concentration too low (ca. 0.01 M) to provide any significant competition with the benzene for light absorption quenches the S₁ → S₀ fluorescence of benzene and replaces it, via energy transfer, with an S₁ → S₀ fluorescence from *p*-terphenyl.¹ Defining a new excitation spectrum variable, β_t(λ), to be the ratio of the fluorescence quantum yields from *p*-terphenyl for excitation of the benzene at wavelength λ to that for excitation at λ₁, it was found that, from λ = 225 to 150 nm, β_t(λ) showed qualitatively the same wavelength variation as β_f(λ), except that their ratio, β_t(λ)/β_f(λ), was somewhat larger than unity and increasingly so in regions where the optical absorptivity of the benzene was largest (i.e., from λ = 185 to 190 nm).^{1,3} Very similar results to these were obtained using 2,5-diphenyloxazole (PPO) instead of *p*-terphenyl.⁵

The possibility of some artifactual cause for the peculiar anticoincidence of the fluorescence action spectra and the optical absorption spectra was considered in all of these early investigations. Thus, as the absorption coefficient increased and the penetration depth of the exciting light accordingly decreased, there would be increasing probability within the lifetime of the fluorescing state (ca. 30 ns for the alkylbenzenes)⁶ for its diffusion to the window–liquid interface. Any quenching, due to some interaction of the excited molecule with the window or with photochemical products at the interface would, perforce, generate the observed anticoincidence. However, that this could not be, at least, the entire origin of the effect was indicated by the fact that the anticoincidence was not much altered by replacing the ca. 30 ns lived S₁ states of the alkylbenzenes with the ca. 1–2 ns lived S₁ states of *p*-terphenyl or PPO.^{1,3,5} Additionally, the effects of dilution of the alkylbenzene with

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saturated hydrocarbons, which, of course, should have significantly increased the penetration depth of the exciting light at the dilutions studied (i.e., 4% by volume), were found to have relatively small effects on the fluorescence excitation spectra, at least, over the spectral range $\lambda = 270\text{--}190\text{ nm}$ ^{1,4} and, indeed, in the case of benzene, to even cause a decrease in $\beta_f(\lambda)$.

The exact extent of the correction required for the "penetration depth" artifact was obtained at one wavelength, $\lambda = 185\text{ nm}$, by Lawson et al.^{7,8} It was shown that the addition of O₂ and CCl₄, both of which strongly reduce the lifetime of S₁ benzene, increased $\beta_f(185)$. As the concentrations of these quenchers approached 0.01 M for O₂ and 0.05 M for CCl₄, $\beta_f(185)$ approached a limiting value independent of the nature of the quencher and of further increase in its concentration. Also, it was reported that on addition of PPO, as its concentration approached 0.01 M, $\beta_f(185)$ also approached a limiting value which, within a few percent, was the same limiting value as had been obtained for $\beta_f(185)$ using O₂ and CCl₄. These limiting values were then interpreted as being the "corrected" S₃ \rightarrow S₁ conversion efficiencies (i.e., corrected for surface quenching by virtue of having adequately reduced the lifetime of the emitting species so as to make such quenching negligible). For neat liquid benzene, this limiting value was 0.45 (as compared to $\beta_f(185) = 0.36$ when all S₁ quenchers were absent). In what follows, we will refer to the corrected quantum yield simply as $\beta(185)$.

Fuchs and Voltz⁹ suggested a possible explanation for the recovery of $\beta_f(\lambda)$ to the blue of ca. 190 nm. Their system was benzene containing α -naphthyl-2-phenyl-5-oxazole (α NPO) at 0.018 M, to which was added chloroform at concentrations from 0.05 to 0.5 M. They monitored the fluorescence of α NPO and reported that the chloroform strongly reduced $\beta(\lambda)$ beginning at a wavelength close to the position of the minimum in $\beta_f(\lambda)$. In view of the known high-electron capture cross-section of chloroform, they suggested that at ca. 7.0 eV (180 nm) there existed a threshold for photoionization of neat liquid benzene. Accordingly, in the absence of chloroform, the recovery in $\beta(\lambda)$ at energies above the threshold was attributed to recombination of the ionized electron (or the negative ion of α NPO) with the benzene positive ion to directly generate the S₁ state of benzene (or of α NPO). Thus would be avoided the inefficient cascade of S₃ to S₁ via the neutral states. This explanation was also adopted by Schwarz and Mautner¹⁰ to account for the effects of chloroform, methyl chloride, and ethyl chloride on $\beta_f(\lambda)$ for neat liquid benzene over an excitation range from 270 to 110 nm. For chloroform and methyl chloride, they observed effects very similar to those obtained by Fuchs and Voltz⁹ (albeit the methyl chloride had less quenching effect than chloroform) but, for ethyl chloride, reported essentially no effect even up to concentrations of 0.9 M.¹¹ Adopting the same point of view as had Fuchs and Voltz,⁹ they suggested electron capture to be the origin of the enhanced quenching beginning, according to their data at ca. 175 nm, and thus set an ionization threshold of neat liquid benzene at 7.1 eV. The absence of an effect for ethyl chloride was considered to be consistent with its smaller capture cross-section for the thermal electrons. In a subsequent paper,¹² these quenching measurements were extended to other alkylbenzenes with similar results to those for benzene.

In neither the work of Fuchs and Voltz⁹ nor of Schwarz and Mautner^{10,12} did these authors address the question of why the upswing in $\beta(\lambda)$ always occurred at significantly lower energies (i.e., at ca. 6.6 eV in benzene) than their suggested ionization thresholds. Additionally, in both sets of measurements, one can see evidence of enhanced quenching by chloroform even at significantly longer wavelengths within the S₀ \rightarrow S₂ absorption

system, and indeed, in somewhat earlier work, Wu¹³ had reported that for dilute solutions of the alkylbenzenes in isooctane the addition of chloroform had its first noticeable effect on $\beta(\lambda)$ well within the S₀ \rightarrow S₂ system. Thus, were the enhanced quenching effects of the alkyl halides due to an ionization threshold, this threshold would have to be set at a much lower energy in dilute solution (e.g., for 4% benzene in isooctane at 6.2 eV). Since these dilute solutions exhibited no minimum in $\beta(\lambda)$ at 6.2 eV,¹⁴ the connection of an ionization with the upswing was somewhat precarious. Additionally, recent photocurrent measurements on neat liquid benzene have reported a photocurrent threshold at an energy of 7.65 eV,¹⁵ significantly above the 6.6 eV position of the minimum, thus mandating the development of a new explanation for the recovery of the fluorescence.

The present investigation was undertaken to reopen the question of the origin of the peculiar features of the benzene liquid fluorescence excitation spectrum and to study how these features develop as the concentration of benzene increases from low to high concentrations. Benzene has had so much spectroscopic attention in recent years that it seemed appropriate to once again attempt to unravel the photophysical properties of its liquid state at high excitation energies. To assist us in this regard, we have recently reexamined the S₀ \rightarrow S₂ and S₀ \rightarrow S₃ absorption spectrum of concentrated solutions of benzene in *n*-hexane¹⁶ and confirm previous surmises that there indeed exists a strong nonartifactual correlation with the fluorescence excitation spectrum. The origin of this mirror-like anticoincidence has not previously been addressed.

II. Experimental Section

Measurements from 270 to 150 nm were made with a Spex F212 spectrofluorometer modified as has been previously described.¹⁷ Samples were illuminated either with a 30 W Hamamatsu L879 D₂ lamp (fitted with a MgF₂ window) or with an electrodeless lamp containing 220 Torr of Xe. The Xe lamp was constructed from a Pyrex tube to which was attached via a Pt/AgCl seal a 1 mm thick LiF window. Power for the lamp was supplied from a 2450 megacycles/s Raytheon microwave generator operating at 25 W. The Xe lamp supplied a continuum from ca. 150 to 190 nm whose intensity, although lower and somewhat less stable than that from the D₂ lamp, had a much slower variation with wavelength. This aspect of the Xe lamp was utilized in a search, albeit negative, for any possible artifacts in the experimental fluorescence excitation spectrum (which is a ratio of two independent scans, one of sample and one of monitor) that might have been caused by the rapid variation in intensity in the D₂ lamp from 155 to 175 nm.

Exciting monochromators were usually run with a band-pass of 1–2 nm, and the analyzers, at ca. 5–10 nm. The sample cells were illuminated at normal incidence, and the fluorescence was collected at an angle of 22.5° from the normal.¹⁷ Sample cells were fitted with 1 mm thick LiF windows connected to the cell body either with Pt/AgCl seals (to Pyrex) or with indium O-rings (to copper). Occasionally, a Suprasil quartz window was used in order to assess contributions from stray excitation light. Such contributions were, however, always found to be of negligible significance.

The intensity of the exciting light was usually monitored with a screen of sodium salicylate that had been sprayed onto the back surface of a LiF¹⁸ window from a saturated solution in absolute ethanol and periodically inserted into the position otherwise occupied by the cell front window. Although the windows for the screen and for the sample cells were chosen to be as similar as possible in their optical transmission, their

similarity was generally lost after some time due to disparity in their aging characteristics. Accordingly, the screens were periodically checked by placing in the sample cell a liquid monitor of either neat *cis*-decalin or neat perhydrophenanthrene and monitoring their fluorescence at ca. 230 nm. The *cis*-decalin has been previously shown to exhibit a fluorescence efficiency which is independent of excitation energy from 120 to 185 nm.¹⁹ Perhydrophenanthrene has been found, in this investigation, to behave similarly but with somewhat higher intensity and over a larger spectral range (120–190 nm).

Corrections have not been applied for reflection losses at the window–solution interfaces. For dilute solutions, these would not be particularly significant, by virtue of our use of *cis*-decalin or perhydrophenanthrene as monitors of the exciting light in the region where such correction would be most important. For the neat liquid, such corrections are more important but still of relatively minor significance. A calculation using the experimental absorption coefficients¹⁶ and refractive indices²⁰ of the neat liquid indicates that corrections for reflection loss never exceed ca. 8% and vary sufficiently slowly that none of the features that we observe in the fluorescence excitation spectrum are significantly affected either in spectral position or in magnitude.

In front face fluorescence measurements, the collection efficiency of the emitted light becomes independent of excitation wavelength only for sufficiently small optical penetration depths. To satisfy this constraint for our system, it was required that the sample's optical absorption coefficient remain above ca. 10 cm⁻¹. From examination of the absorption spectrum of benzene,^{2,16,21} it follows that this constraint is satisfied for all solutions that we have studied for excitation wavelengths $\lambda < 217$ nm and at all λ for benzene concentrations greater than ca. 1.5 M. At lower concentrations and longer excitation wavelengths, our measured fluorescence intensity at selected values of λ will be too low by virtue of inadequate collection efficiency. This, however, is only a problem in the region of very low optical absorptivity between the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ absorption systems from ca. 230 to 217 nm. Although no formal corrections were made for these effects, they have been qualitatively considered in interpretations of the pertinent excitation spectra.

All fluorescence intensities were monitored at a single wavelength of the fluorescence spectrum either at the fluorescence maximum or (in the case of examination of the fluorescence of the saturated hydrocarbons when benzene was added to them) sufficiently to the red of the emission maximum so as to avoid any attenuation of the solvent fluorescence by the benzene. Although monitoring was done at a single wavelength, this was always preceded by a sweep of the emission spectrum to confirm its reliability.

Unless otherwise specified, all measurements were made at 20 °C on nitrogenated solutions. For some preliminary measurements at lower temperatures, cooling was accomplished using precooled gaseous N₂ as heat exchanger. The temperature control was ± 2 °C for periods sufficiently long for a reliable sweep of the excitation monochromator (ca. 20 min).

Benzene (Omnisolve, glass distilled), *n*-hexane (Mallinckrodt, spectrophotometric grade), and isooctane (American Burdick and Jackson, high purity solvent) were usually used without purification after establishing that additional treatment²² had no significant effect on the fluorescence excitation spectra. Both *cis*-decalin (Aldrich, 99%) and perhydrophenanthrene (Chemicals Procurement Inc.) were additionally purified by percolation through activated silica gel. All other chemicals employed in this investigation were purchased in high purity and usually

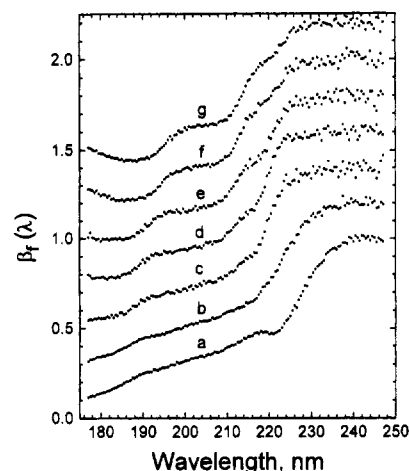


Figure 1. Fluorescence excitation spectra from 180 to 250 nm of benzene in *n*-hexane at concentrations of (a) 0.11₂ M, (b) 0.22₄ M, (c) 1.1₂ M, (d) 2.2₄ M, (e) 4.4₈ M, (f) 8.9₆ M, and (g) 11.2 M (neat liquid). The ordinate of spectrum a is shown correctly but spectra b–g are each successively shifted upward by 0.20 ordinate units.

employed without further treatment. Absorption spectra to 170 nm were obtained with a Cary 15 spectrophotometer, and those to shorter wavelengths, with a McPherson (230 S) 1 m vacuum monochromator in conjunction with a McPherson (665) double-beam attachment.

III. Results

As has been previously reported,¹ the emission spectrum of benzene (over both monomer and excimer bands)^{23–25} was found to be invariant to excitation wavelength except for slight reabsorption effects. These were manifested only on the short-wavelength edge of the emission spectrum (and only over a rather narrow band of excitation wavelengths that are weakly absorbed within the $S_0 \rightarrow S_1$ system). The fluorescence excitation spectra were therefore monitored using analysis wavelengths sufficiently to the red of this edge to avoid the reabsorption.

Figure 1 shows the fluorescence excitation spectra of benzene for a series of representative solutions in *n*-hexane from 0.11₂ to 11.2 M (neat liquid benzene) over an excitation spectral range from $\lambda = 250$ to 190 nm. For convenience of presentation, each spectrum has been successively shifted upwards by 0.10 ordinate units. All spectra have been normalized to unity at the wavelength of maximum $S_0 \rightarrow S_1$ optical absorptivity ($\lambda = 254$ –255 nm). At this wavelength, the decadic optical absorptivity, $k(\lambda)$, of benzene even in the 0.11₂ M solution (where $k(254) = 250$ M⁻¹ cm⁻¹)²¹ is adequately large to ensure complete light absorption within the viewing geometry of our collection system. However, at shorter wavelengths within the $S_0 \rightarrow S_1$ band this is no longer the case. The average absorptivity on this edge slowly declines, ultimately reaching in the spectral region between the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ absorption systems a minimum value of $k(222) = 6$ M⁻¹ cm⁻¹ in dilute solutions²¹ and of $k(227) = 15$ M⁻¹ cm⁻¹ in the neat liquid.^{2,16} Since saturation of our viewing geometry is not complete until the absorption coefficient is 10 cm⁻¹, fluorescence intensities in this region will tend to be too low until benzene concentrations of ca. 1.5 M are reached. However, to the blue of 217 nm (and between 232 and 267 nm), the viewing geometry was saturated at all concentrations shown in Figure 1. Although not shown here, measurements at lower concentrations from 0.0089₆ to 0.11₂ M were found to be independent of benzene concentration between 180 and 200 nm.

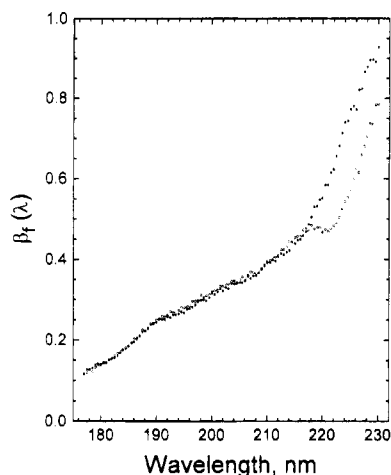


Figure 2. Fluorescence excitation spectra from 180 to 230 nm of benzene in *n*-hexane at concentrations of 0.11₂ M (open circles) and 0.22₄ M (filled circles).

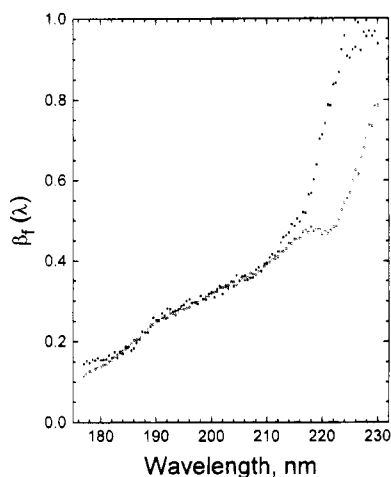


Figure 3. Fluorescence excitation spectra from 180 to 230 nm of benzene in *n*-hexane at concentrations of 0.11₂ M (open circles) and 1.1₂ M (filled circles).

Figures 2–5 show a direct comparison (on the same ordinate scale) of the excitation spectra of benzene in *n*-hexane from 180 to 230 nm at selected concentration pairs. These figures are presented to facilitate our subsequent discussion of certain features in the spectra and their change with concentration.

Fluorescence excitation spectra of benzene in *n*-hexane in the shorter wavelength regime from 150 to 190 nm are exhibited in Figure 6A at some representative concentrations ranging from 0.0089₆ to 11.2 M. Except at the lowest concentrations of 0.0089 M, the spectra were all normalized, as in Figure 1, to unity at 255 nm. For the 0.0089₆ M solution, the normalization was to the value of $\beta_f(\lambda) = 0.208$ at 187 nm. For all solutions, and over the entire spectral range shown in Figure 6A, the viewing geometry remains constant.

The first three spectra in Figure 6B (labeled a, b, and c) are simply expanded versions of some of the spectra in Figure 6A to show more clearly the development of certain structures in the fluorescence excitation spectrum as the benzene concentration increases from 0.56 to 2.2 M. The spectrum labeled d in Figure 6B is the fluorescence excitation spectrum of 0.014 M PPO in a 2.2 M solution of benzene in *n*-hexane. In this case, the fluorescence of the PPO rather than that of the benzene has been monitored. The PPO concentration is sufficiently low in this solution that all of the incident light is absorbed by the benzene in the spectral region from 150 to 190 nm. The

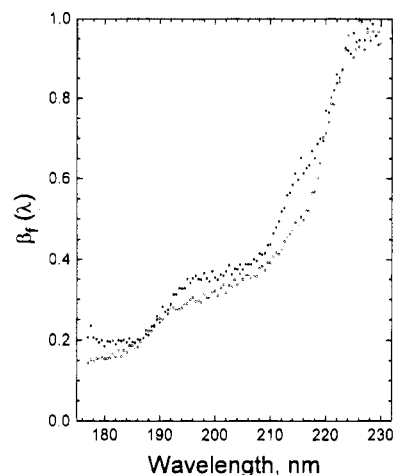


Figure 4. Fluorescence excitation spectra from 180 to 230 nm of benzene in *n*-hexane at concentrations of 1.1₂ M (open circles) and 4.4₈ M (filled circles).

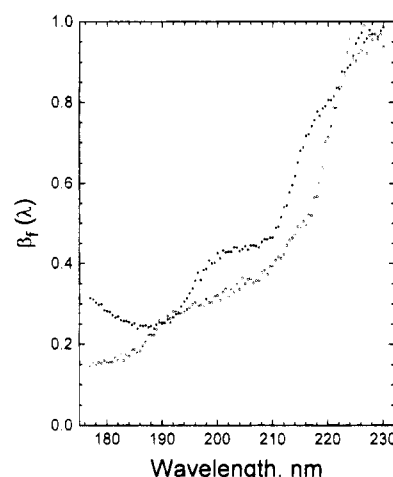


Figure 5. Fluorescence excitation spectra from 180 to 230 nm of benzene in *n*-hexane at concentrations of 1.1₂ M (open circles) and 11.2 M (filled circles).

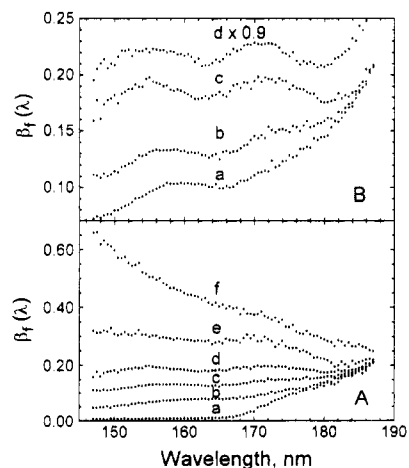


Figure 6. Fluorescence excitation spectra from 150 to 180 nm of benzene in *n*-hexane solutions. A: (a) 0.0089₆ M benzene; (b) 0.22₄ M benzene; (c) 1.1₂ M benzene; (d) 2.2₄ M benzene; (e) 8.9₆ M benzene; (f) 11.2 M benzene (neat liquid). B: (a) 0.56₀ M benzene; (b) 1.1₂ M benzene; (c) 2.2₄ M benzene; (d) 0.01₄ M PPO (containing 2.2₄ M benzene).

normalization of spectrum d in Figure 6B is to unity at 255 nm. However in the spectral region around 255 nm there is sufficient absorption by the PPO to make somewhat ambiguous the propriety of this normalization. Nevertheless, as will be

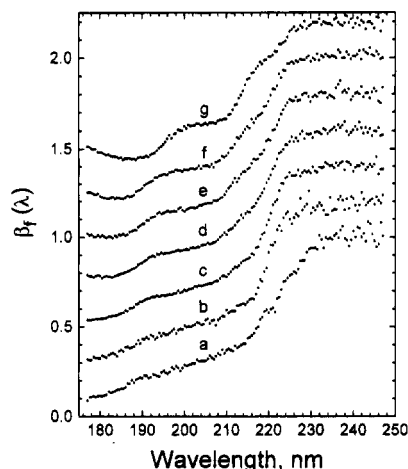


Figure 7. Fluorescence excitation spectra from 180 to 250 nm of benzene in isooctane at concentrations of (a) 0.224 M, (b) 0.560 M, (c) 1.12 M, (d) 2.24 M, (e) 4.48 M, (f) 6.72 M, and (g) 11.2 M (neat liquid). The ordinate of spectrum a is shown correctly but spectra b–g are each successively shifted upward by 0.20 ordinate units.

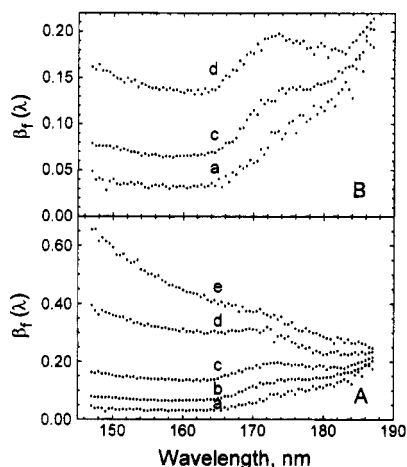


Figure 8. Fluorescence excitation spectra from 150 to 190 nm of benzene in isooctane. A: (a) 0.560 M; (b) 1.12 M; (c) 2.24 M; (d) 6.72 M; (e) 11.2 M. B: (a) 0.560 M; (c) 1.12 M; (d) 2.24 M.

discussed later, our major purpose in displaying the PPO spectrum here is to show the similarity of its structural features to those of spectrum c. A very weak benzene emission was also observed from the PPO solution with a fluorescence excitation spectrum essentially the same as that of PPO when normalized to the PPO spectrum at 190 nm.

A similar series of experiments to those cited above were performed with isooctane solutions of benzene. From 180 to 250 nm, the fluorescence excitation spectra shown in Figure 7 are very similar to those obtained in *n*-hexane except at concentrations above ca. 4 M, for which there is observed a ca. 5–10% increase in $\beta_f(\lambda)$ in the region around $\lambda = 190$ nm. This increase is considered to be merely an artifact of a reduced surface quenching in the isooctane due to its somewhat higher viscosity. Significant differences between isooctane and *n*-hexane were, however, observed to the blue of 180 nm. Figure 8 shows some representative fluorescence excitation spectra of benzene in isooctane in this shorter wavelength spectral region. The normalization is again to unity for excitation at 255 nm for all solutions.

A few measurements were also made using the solvents *n*-pentane, cyclohexane, and *cis*-decalin. In the case of *n*-pentane, results almost identical to those in *n*-hexane were obtained over the entire spectral region from 150 to 270 nm and at all concentrations. For both cyclohexane and *cis*-decalin,

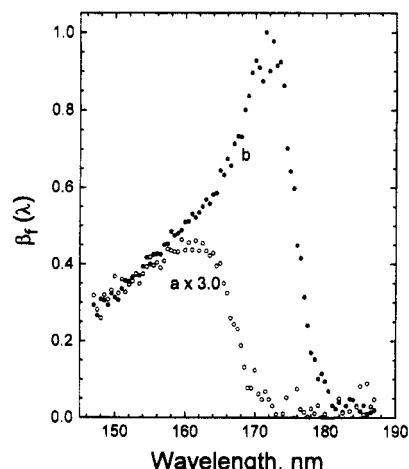


Figure 9. Fluorescence excitation spectra from 150 to 190 nm of *n*-hexane (a) containing 0.112 M benzene in hexane and (b) without benzene. Spectrum b has been normalized to unity at 172 nm. Spectrum a when divided by 3.0 is correct relative to spectrum b.

above ca. 1 M, the fluorescence excitation spectra in the spectral region to the red of 190 nm were essentially the same as those in *n*-hexane except for a ca. 10–30% increase in $\beta_f(\lambda)$ attributable again (as in isooctane) to the effect of increasing viscosity to reduce the effect of the surface quenching. The spectral region below 190 nm, however, was complicated by relatively strong solvent absorption of the exciting light and subsequent transfer of the excitation energy to benzene. Detailed studies of this transfer process have been presented elsewhere.^{17,26}

Figure 9 shows the intensity of *n*-hexane fluorescence as a function of excitation energy in the presence and absence of 0.112 M benzene (curves a and b, respectively). Complete light absorption by the neat solvent within the region of our maximal collection efficiency is achieved at ca. 172 nm. The addition of benzene (as indicated in spectrum a) blue shifts this wavelength, and the ratio of the a to b spectra would be the fraction of exciting light that is absorbed by the hexane in the presence of the 0.112 M benzene were it not for a quenching action of the benzene on the hexane fluorescence (due to hexane to benzene energy transfer). To correct for this quenching effect, the “a” curve has been multiplied by the indicated factor of 3.0 in Figure 9. This factor was empirically chosen to cause the a and b curves to become coincident below 155 nm, where we expect the solvent in the 0.11 M solution to absorb essentially all of the incident light. A simple analysis of the energy transfer kinetics shows that the reciprocal of this normalizing factor (i.e. 0.33) must be the probability that excited *n*-hexane is not quenched by 0.112 M benzene.¹⁷ A similar treatment of the data for cyclohexane and *cis*-decalin, although not shown here, gave quenching probabilities in good agreement with those previously reported.^{17,26}

Granting the validity of the above procedure, it would be expected that the fraction of light absorbed by the hexane should be obtained from the ratio of the ordinate of the normalized a curve to that of the b curve. This is indeed the case. For example, we find from Figure 9 that at $\lambda = 170$ and 166 nm ca. 11% and 48% of the light within our excitation band-pass is absorbed by the *n*-hexane in the 0.112 M benzene solution. The value at 170 nm is in reasonable agreement with a 9% value obtained from measured optical absorptivities of neat *n*-hexane ($k = 10 \text{ M}^{-1} \text{ cm}^{-1}$) and of 0.112 M benzene in *n*-hexane ($k = 7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁶ Also, at 166 nm, it is close to a value of 49% obtained by using a measured optical absorptivity for *n*-hexane of $k = 85 \text{ M}^{-1} \text{ cm}^{-1}$ and an estimated value for

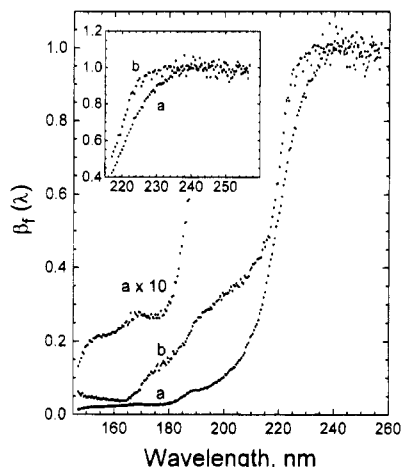


Figure 10. Fluorescence excitation spectra from 150 to 260 nm of 0.560 M benzene in (a) *n*-perfluorohexane and (b) isooctane. The inset shows an expanded view of the region from 220 to 260 nm.

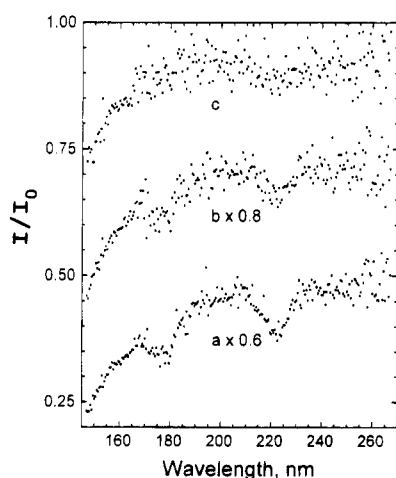


Figure 11. Ratio of the fluorescence intensity from neat liquid benzene in the presence of chloroform (I) to that in its absence (I_0) as a function of excitation wavelength from 150 to 260 nm for chloroform concentrations of (a) 0.5 M, (b) 0.25 M, and (c) 0.12 M. The data at 0.25 and 0.5 M are displaced downward by 25 and 67%, respectively.

benzene of $k = 6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ (obtained via extrapolation of a dilute solution spectrum).¹⁶ Unfortunately, these measurements could not be extended to higher benzene concentrations due to the weakness of the *n*-hexane emission.

In Figure 10 we show a comparison of the fluorescence excitation spectra of 0.560 M benzene in the solvents *n*-perfluorohexane (curve a) and isooctane (curve b) in the spectral region from 150 to 260 nm. The concentration of 0.560 M is close to the solubility limit of benzene in *n*-perfluorohexane at 20 °C. The *n*-perfluorohexane was chosen in order to examine the effects of a solvent in which the photophysical properties of benzene (with regard to both absorption and fluorescence) have been reported to be almost vapor-like.⁸

Some neat liquid benzene action spectra were determined in the presence of low concentrations of chloroform. Figure 11 shows these results for chloroform concentrations of 0.12, 0.25, and 0.50 M. The ordinate is the ratio of the fluorescence intensity of the benzene in the presence of the additive (I) to that in its absence (I_0) as a function of excitation wavelength. For clarity of presentation, the curves for 0.25 and 0.50 M chloroform are displaced downward by 25% and 67%, respectively.

Figure 12A shows a comparison of the fluorescence excitation spectrum of neat liquid benzene with and without 0.014 M 2,5-

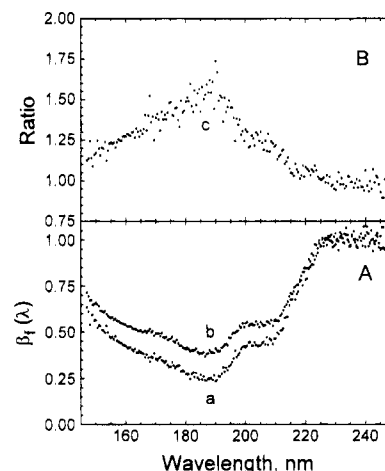


Figure 12. A: Fluorescence excitation spectrum from 180 to 250 nm (a) of neat liquid benzene and (b) of PPO at a concentration of 0.014 M in liquid benzene. B: Ratio of spectrum b to spectrum a.

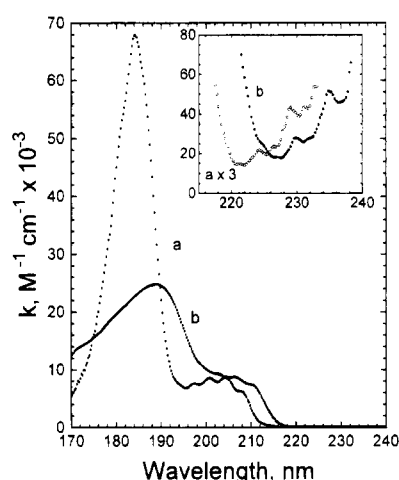


Figure 13. Electronic absorption spectrum from 170 to 240 nm of (a) 0.0090 M benzene in *n*-hexane and (b) neat liquid benzene. Inset shows the same spectra in the region from 215 to 240 nm.

diphenyloxazole (PPO). The spectrum with PPO present was obtained by monitoring the PPO fluorescence. Increasing the concentration of PPO to 0.03 M gave identical results to those at 0.014 M, as had been previously reported for measurements at a single excitation wavelength of 185 nm.^{7,8} At both PPO concentrations, the excitation light is absorbed exclusively by the benzene. In Figure 12B, we show the ratio of the excitation spectrum with PPO to that without.

For the convenience of the following discussion, we present in Figure 13 absorption spectra of neat benzene and of a dilute solution (0.01 M) of benzene in *n*-hexane that span the spectral region covering the second and third valence absorption systems.¹⁶ In the inset to this figure, we provide an expanded view of the region between the first and second absorption systems.

IV. Discussion

A. Fluorescence Excitation Spectrum of Benzene for Excitations within the First Absorption System. The $S_0 \rightarrow S_1$ absorption band of dilute solutions of benzene in saturated hydrocarbon solvents spans a spectral region from ca. 270 to 225 nm. The oscillator strength of the band is very weak, with a maximum decadic absorptivity of $k = 250 \text{ M}^{-1} \text{ cm}^{-1}$ at 254 nm and a minimum of $k = 6 \text{ M}^{-1} \text{ cm}^{-1}$ at 223 nm.²¹ As the benzene concentration increases, this band red shifts but only

very slightly as compared to the next higher transition ($S_0 \rightarrow S_2$).^{2,16} Accordingly, in the neat liquid, the wavelength of minimum absorptivity red shifts by ca. 3 nm to 227 nm and k increases to $14 \text{ M}^{-1} \text{ cm}^{-1}$ (see Figure 13).

Recalling that our optical geometry requires a minimum absorption coefficient of about 10 cm^{-1} to provide wavelength invariant collection efficiency, we find that at ca. 1 M (see Figure 1c) our viewing geometry becomes finally "saturated", and we observe that, starting here and continuing to higher concentrations, the benzene fluorescence excitation spectrum remains essentially constant from 270 to $224 \pm 1 \text{ nm}$ in the 1.1 and 2.2 M solutions and to $226 \pm 1 \text{ nm}$ in the more concentrated solutions. In more dilute solutions, there is a premature falloff in the spectrum due to the incomplete absorption within our viewing geometry. Similar results were obtained in isooctane (see Figure 7) and in all other saturated hydrocarbon solvents studied here.

This constancy of the fluorescence excitation spectrum for excitations within the first absorption system of benzene in hydrocarbon solvents is well-known.²⁴ It stands in sharp contrast, however, to the behavior of benzene vapor, for which the $S_0 \rightarrow S_1$ fluorescence intensity suddenly "disappears" for excitations at ca. 240 nm (i.e., 0.42 eV above the vapor absorption onset).^{24,27} The mechanism responsible for this disappearance of fluorescence, the so-called "channel 3" mechanism, remains unknown but appears to involve nonradiative transition to the ground state via some unknown surface.²⁷ Whatever its nature, however, it appears to be unable to effectively compete with the rapid vibrational redistribution and relaxation processes that prevail in a saturated hydrocarbon liquid.

For benzene in *n*-perfluorohexane, however, the situation appears somewhat altered. Figure 10 shows a comparison of the fluorescence excitation spectra of 0.560 M benzene in isooctane and in *n*-perfluorohexane, and as is clear from the inset, the fluorescence excitation spectrum begins its descent in the perfluorocarbon at a significantly longer wavelength (240 nm) than in isooctane. Since the benzene absorption coefficient stays above 10 cm^{-1} from 265 to 231 nm in the perfluorohexane, the decline at 240 nm cannot be considered artifactual. On the other hand, in the isooctane, the absorption coefficient in the region between 231 and 225 nm varies from ca. 4.5 to 9 cm^{-1} , which is somewhat below the optical density required to saturate our viewing geometry. Accordingly, in isooctane, the fluorescence excitation spectrum begins a premature decline in 230 nm in the 0.560 M solution rather than at 224 nm (the saturation value at 1 M). Thus the disparity in onsets of the decline of the fluorescence in the two solvents is even larger than apparent in Figure 10.

As has been previously reported, both the absorption and emission spectra of benzene in *n*-perfluorohexane behave almost vapor-like both in their spectral position and in their spectral sharpness.^{8,28} With this in mind, it is perhaps not unexpected to find that the fluorescence excitation spectrum, at least within the region of the $S_0 \rightarrow S_1$ band, also behaves vapor-like in this solvent and begins its decline at almost the same wavelength as it does in the vapor phase and is, most plausibly, a manifestation of the same channel 3 behavior.

B. Fluorescence Excitation Spectrum of Benzene for Excitations within the Second Absorption System. At about 224–226 nm, which marks the entrance into the benzene $S_0 \rightarrow S_2$ absorption system (depending on concentration as indicated in Figure 13), the benzene fluorescence quantum yield drops sharply (see Figures 1 and 7). Although somewhat obscured by inadequate optical absorptivity in the more dilute solutions,

a crude correction for this indicates the falloff to persist even at the lowest concentration we have studied of 0.0089₆ M. Entirely similar behavior was obtained in *n*-pentane, cyclohexane, and *cis*-decalin.

Although the decadic absorptivity of the benzene rapidly increases over the same spectral region in which is observed the decline in $\beta_f(\lambda)$, the falloff (at least in major part) cannot be attributed to penetration depth artifacts. This is most immediately apparent from the fact that at 214.5 nm the decadic absorptivity of benzene in dilute hydrocarbon solution²¹ becomes about equal to that at the peak of the $S_0 \rightarrow S_1$ transition (i.e. $k = 250 \text{ M}^{-1} \text{ cm}^{-1}$ at 254 nm), and yet, from Figure 1 we note that $\beta_f(\lambda)$ has already dramatically declined by this wavelength. Also, in the neat liquid, where now even at 218.5 nm the optical absorptivity has reached a value comparable to that at the peak of the $S_0 \rightarrow S_1$ transition ($k = 220 \text{ M}^{-1} \text{ cm}^{-1}$ at 255 nm),^{2,16} there has also been achieved a rather low value of $\beta_f(\lambda)$.²⁹

The origin of this rapid falloff at 224–226 nm has never been theoretically addressed. As is well-known, there is no evidence for compensating benzene photochemistry nor for intersystem crossing to the triplet.^{1,24} The situation, therefore, is not unlike that which led, in the vapor phase, to the conjecture of a channel 3 opening at 240 nm and suggests that in saturated hydrocarbon liquids this opening is simply delayed to shorter wavelengths. If we adopt the usual theoretical point of view that channel 3 involves radiationless transitions at an intersection of S_1 with some unknown surface S_x and of S_x with S_0 ,^{27,28} then it would appear that the presence of a saturated hydrocarbon bath, although able to prevent the $S_1 \rightarrow S_x \rightarrow S_0$ process, cannot similarly prevent S_2 from ultimately decaying to S_0 .

A possible explanation for this follows from a recent suggestion by Sobolewski³⁰ that S_x is to be identified with S_2 and that it is an intersection of S_2 with S_1 at the channel 3 opening and its further intersection with S_0 along a path of valence isomerization that lead ultimately to the loss of $S_1 \rightarrow S_0$ fluorescence. Accordingly, we would expect that for direct excitation into S_2 there would remain a high probability to remain on the S_2 surface until its intersection with S_0 . Also, since the falloff in $\beta_f(\lambda)$ persists essentially unabated (albeit with declining slope) throughout the $S_0 \rightarrow S_2$ absorption band to ca. 195 nm (at least in the more dilute solutions), it would appear that as more and more energy is imparted to the S_2 excitation packet, the probability for it not to cross at the S_2 – S_1 intersection must increase (as would be qualitatively expected from a simple Landau–Zener formulation of the crossing rate).³¹

For concentrations of benzene below 1 M, the fluorescence excitation spectrum over the entire $S_0 \rightarrow S_2$ absorption system (from 224 to 191 nm)³² appears to be essentially independent of benzene concentration³³ (see Figure 2). There is a sudden falloff in fluorescence at 224 nm and then a slowdown in the rate of decline as the excitation wavelength sweeps to the blue of ca. 215 nm and into the major part of the $S_0 \rightarrow S_2$ system. At benzene concentrations above 1 M, the fluorescence excitation spectrum begins to develop a concentration dependence and two new features appear. The most obvious one is a region of decreased slope that starts rather abruptly at ca. 209–211 nm (depending on the benzene concentration) and continues to ca 191–199 nm. This can be seen faintly in Figure 3, which compares 0.11₂ and 1.1₂ M solutions, is more obvious in 2.2₄ M solutions in Figures 1d and 7c, and in Figure 4 has developed into an almost plateau-like region at 4.4₈ M that persists to the neat liquid in Figure 5. The region in which this occurs (which slowly shifts to the red as the benzene concentration increases), coincides almost exactly with the region of maximum absorp-

tivity of the $S_0 \rightarrow S_2$ system (see Figure 13).^{2,16,21} We will refer to this feature as the " S_2 plateau".

Additional to this, it will be noted in Figures 3–5 that, as the " S_2 plateau" becomes better defined, a "shoulder" begins to appear in the fluorescence excitation spectrum in the region 215–218 nm. This is only faintly discernible at 1.12 M but, as the concentration increases, becomes more and more apparent while slowly shifting to the red, ultimately reaching a wavelength of 218 nm in the neat liquid. Although we shall refer to this feature as a "shoulder", it is, of course (as for the feature we have referred to as the " S_2 plateau"), simply a region of reduced rate of decline in $\beta_f(\lambda)$. These same features have been observed to develop in the same spectral regions and at about the same concentrations in all other saturated by hydrocarbon solvents that we have studied.

The "shoulder" lies on the long-wavelength edge of the $S_0 \rightarrow S_2$ absorption system and may simply signify the existence of another state in this region that successfully competes with S_2 (i.e. B_{1u}) for light absorption and is better coupled to S_1 . However, we have carefully examined the absorption spectrum of neat liquid benzene and of concentrated solutions of benzene in *n*-hexane¹⁶ on the long-wavelength edge of the $S_0 \rightarrow S_2$ transition in order to seek evidence of some structure that develops at these higher concentrations but have found only a rather smoothly increasing rise in optical absorptivity. Shinohara and Nishi³⁴ have recently suggested that for small vapor clusters of benzene there may exist in the region 212–219 nm optical transitions to excited van der Waals dimer states that rapidly convert to an excited B_{2g} excimer state (hereafter referred to as E_1). They observed that whereas the monomeric benzene multiphoton ionizes with very low efficiency when excited in the region from 212 to 219 nm, much higher efficiencies are obtained for small vapor clusters of benzene and conjectured that the E_1 excimer state might be sufficiently longer-lived than the S_2 (i.e. B_{1u}) monomeric state to permit the absorption of the second photon. Their observation is not unrelated to ours. We both observe in the same spectral region of excitation and only at high benzene concentrations what appears to be a loss of coupling of S_2 with S_0 . This leads, in their case, to an ionization efficiency that is anomalously high and, for us, to a sudden reduction in the rate of decline of fluorescence efficiency. To accommodate their explanation to our case, we would additionally have to require that the E_1 excimer decays to $S_1 + S_0$ monomeric states either directly or, alternatively, via the lowest, E_0 (B_{1g}), excimer state (i.e. $E_1 \rightarrow E_0 \rightarrow S_1 + S_0$).

As the excitation wavelength sweeps to the blue of the region of the "shoulder", $\beta_f(\lambda)$ continues its descent at a rate not too disparate from that observed in more dilute solutions (see Figures 3 and 4). Presumably, the excimer precursor states can now no longer compete for absorption of light with direct $S_0 \rightarrow S_2$ monomeric transitions as these begin to develop their intensity. However, at about 210 nm, where the absorption intensity is about 70% of its maximal value in the $S_0 \rightarrow S_2$ system, the region that we have referred to as the " S_2 plateau" begins with a rather abrupt decrease in the rate of decline of the fluorescence excitation spectrum that continues now for at least 10–20 nm (depending on concentration). Since the absorption spectrum of benzene in the region of the $S_0 \rightarrow S_2$ transition seems to be independent of the benzene concentration¹⁶ (except for some red shift as indicated in Figure 13), it seems most reasonable to seek an explanation for the plateau that is initiated by direct transitions to the same S_2 states that are available at the lower concentrations.

The onset of the " S_2 plateau" although appearing to occur at a wavelength imbedded rather deeply within the $S_0 \rightarrow S_2$

absorption system (at ca. 210 nm), in fact, lies close to where we would estimate the position of the origin transition. This follows from the observation that in thin films of solid benzene the 0–0 transition of the $S_0 \rightarrow S_2$ absorption system, forbidden in the D_{6h} geometry, appears weakly at 215 nm.^{35,36} Since the energy difference between this and the most intense vibronic transition of the system (i.e. at 208.5 nm in the solid^{35,36} and 207 nm in the neat liquid^{2,16}) should not be much affected by a change in phase, we would predict for the neat liquid an origin at about 213 nm (shifting to ca. 210 nm in dilute solution in *n*-hexane).¹⁶ Thus it would appear that the effect of increasing benzene concentration to cause development of the " S_2 plateau" requires direct transitions to vibronic states of S_2 that lie above its origin.

In dilute hydrocarbon solutions at 20 °C, the benzene $S_0 \rightarrow S_2$ absorption system clearly begins at a wavelength not less than 222 nm. The fraction of the total system oscillator strength that lies in the 0.32 eV interval between 222 nm and the 0–0 at 210 nm of ca. 6% appears somewhat high to be due entirely to "hot" transitions. Additionally, preliminary measurements on the temperature dependence of the optical absorptivity in this region seem inadequate for such an explanation. To accommodate this discrepancy and, at the same time, to explain the fluorescence action spectrum, we suggest that there exists important contributions to the absorption in this region from "nonvertical" transitions³⁷ to regions of the S_2 surface that are distorted from hexagonal symmetry along the valence isomerization coordinate. The excitation packets thus formed would be expected to move very rapidly to the S_2 – S_1 and S_2 – S_0 intersections and to be relatively unaffected by the presence of neighboring, unexcited benzene. It is these transitions, we suggest, that are responsible for the rapid falloff in the fluorescence excitation spectrum between 224 and 210 nm at all benzene concentrations. At high benzene concentrations the transitions to the aforementioned pre-excimer states begin to compete for light absorption and thus generate the observed "shoulder" but apparently can compete successfully only on the long-wavelength side of the 224–210 nm interval.

To explain now the origin of the " S_2 plateau", it is required that the states of S_2 that are accessed by the "vertical" transitions to the blue of 210 nm have available to them other and more efficient channels for populating S_1 . A simple explanation for this is that the terminal states of such excitations would be expected to retain their saddle point, hexagonal geometries for a sufficient time to permit them to more effectively couple with S_1 . This coupling would, perforce, be intramolecular at the lower concentrations of benzene (i.e. < 1 M) but would be supplemented by intermolecular channels at the higher benzene concentrations via formation of excited excimers. In this way, we would utilize the same basic explanation for the concentration development of the " S_2 plateau" as was utilized for the "shoulder", namely the opening up at high benzene concentrations of excimer channels that are more strongly coupled to S_1 (and/or E_0). The lifetime of S_2 benzene of ca. 40 fs,^{38,39} although too short for diffusional formation of excimers at low benzene concentrations, may, nevertheless, be adequate at the concentrations required. From Figures 3 and 4 it is clear that the fluorescence excitation spectrum in the region from 210 to 191 nm only begins to faintly depart from its concentration invariant value at concentrations in excess of ca. 1 M and is only first fully developed into what we refer to as the " S_2 plateau" at about 2 M. At this latter concentration, the probability of finding a benzene within a 3.5 Å contact distance of S_2 is 20%, which is about what we find for the maximum difference between $\beta_f(\lambda)$ for the 0.11 and 2.2 M solutions (ca. 18%).

C. Fluorescence Excitation Spectrum of Benzene for Excitations within the Third Absorption System. 1. 191–170 nm. Beginning at about 191 nm in dilute saturated hydrocarbon solutions, there appears in benzene its most intense valence transition $S_0 \rightarrow S_3$ ($A_{1g} \rightarrow E_{1u}$) with oscillator strength close to unity.⁴⁰ The optical absorptivity rises rapidly with decreasing wavelength, reaching a maximum decadic absorptivity at 184 nm of $6.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, and then declines to a value of $6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 170 nm.¹⁶ In the neat liquid, this transition is strongly altered. It shifts red, beginning at about 200 nm and rises much less rapidly than in the dilute solution to a maximum decadic absorptivity of only $2.5 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 189 nm.^{2,16} It then slowly declines to a value of $1.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 170 nm.^{2,16} Despite this extensive redistribution of the differential oscillator strength in the neat liquid, its integral over the entire absorption system is essentially unaltered from that of the dilute solution.¹⁶

At wavelengths coincident with or very close to the $S_0 \rightarrow S_3$ absorption onset (at ca. 191 nm in dilute hydrocarbon and 188 nm in dilute perfluorocarbon solutions and shifting to 199 nm in the neat liquid), the fluorescence excitation spectrum of benzene suddenly begins an increase in rate of decline (see Figures 1–8). The break in slope cannot be attributed to a surface quenching artifact, since we observe it even in solutions sufficiently dilute that less than 1% of the absorbed light lies within a diffusion distance accessible to excited benzene. Nor can the effect be attributed to solvent absorption of light, since in this region there is essentially no absorption by the perfluorocarbon and, even at a concentration of benzene as low as 0.2 M, *n*-hexane absorbs less than 0.01% of the incident light at 190 nm. The conclusion is that on entry into S_3 , as was true for entry into S_2 , there occurs a sudden reduction in fluorescence. Also, it should be noted that in both cases this falloff is observed at all benzene concentrations.

In dilute hydrocarbon solutions, of 0.2 M or less, the falloff continues smoothly to about 170 nm (see Figures 6 and 8), but as the benzene concentration increases, there begins to develop at ca. 0.5 M a halt in the rate of decline and then, starting at about 1 M, a turnaround in $\beta_f(\lambda)$ and a recovery of fluorescence (see Figures 3–8). The halt begins at ca. 187 nm in a 0.56 M solution in *n*-hexane and shifts to 193 nm in the neat liquid. The minimum is first observed at $\lambda = 182 \text{ nm}$ in the 1.1 M solution and shifts to $\lambda = 188 \text{ nm}$ in the neat liquid (Figures 1 and 3), maintaining always a position close to the absorption maximum of the $S_0 \rightarrow S_3$ system¹⁶ albeit very slightly shifted to the blue. The similarity in structure of the spectrum in this spectral region with and without PPO present (see Figure 12 and section V.C) essentially dismisses the possibility of a surface quenching effect as an explanation for the turnaround.

The falloff in the onset region of the $S_0 \rightarrow S_3$ absorption system is strikingly similar in appearance to that which occurs just prior to the 0–0 transition of the $S_0 \rightarrow S_2$ system. This is particularly obvious when the fractional changes in $\beta_f(\lambda)$ per electronvolt are compared for the two regions. The most obvious implication, then, is that similar mechanisms are operating in the two spectral regions. Thus we suggest for $S_0 \rightarrow S_3$, as we did for $S_0 \rightarrow S_2$, that excitations on the long-wavelength edge of the absorption system generate “non-vertical” states³⁷ similarly distorted along some valence isomerization coordinate and that these are so efficiently coupled to S_0 (either directly or, more plausibly, via S_2) as to lead always to rapid reduction in fluorescence at all benzene concentrations.

In our explanation of the “ S_2 plateau” at high benzene concentrations, we were constrained by the observation that the $S_0 \rightarrow S_2$ absorption spectrum itself was relatively unaltered by

changing the benzene concentration.¹⁶ Accordingly, we concluded that the terminal states of this absorption in the spectral region where the plateau is observed were “vertical” localized S_2 states that only subsequently evolved into excimeric states. To explain, however, the “ S_3 plateau” (and its subsequent upswing at higher benzene concentrations), this constraint disappears. The very intense $S_0 \rightarrow S_3$ absorption spectrum undergoes such profound modifications as the benzene concentration increases that transitions to states of increasingly collective nature must be considered.¹⁶ Certainly, for sufficiently extended states (as has been suggested in other contexts),^{41,42} there is expected to be a reduction in the magnitude of the “force” impelling the system to distort away from its ground state equilibrium nuclear configuration. For the benzene system, this could permit an $S_3 \rightarrow S_2 \rightarrow S_1$ channel (utilizing configurations with the hexagonal geometry of the ground state) to so successfully compete with motion along the distortion coordinate as to cause the observed recovery of the fluorescence.

The suggestion that collective components develop in the $S_0 \rightarrow S_3$ absorption spectrum as the benzene concentration increases is not new. Frenkel excitons have already been invoked by Brith, Lubart, and Steinberger⁴³ to explain the intensity distribution in the absorption spectrum of thin films of solid benzene utilizing calculations of Craig and Walsh⁴⁴ that summed transition dipoles over a sphere of at least 20 Å extent. Also, for the neat liquid, charge transfer excitons (albeit in a more localized form as benzene–benzene charge transfer complexes) have been suggested by Scott, Braun, and Albrecht⁴⁵ to explain a peculiar temperature dependence of the benzene 2-photon absorption spectrum that begins at 197 nm. More recently, Schriver, Hahn, and Whetten⁵¹ have reported that irradiation at 193 nm of large clusters of benzene vapor results in efficient ionization at anomalously low fluences. Their explanation is based on a model involving the diffusion of excitons to neighboring sites and then their fusion to form states above the ionization threshold. Although they envisioned for this model an energy transport via S_1 excitons produced by internal conversions from localized S_3 states, it would not detract from their basic view were the initial S_3 excitations to be of a more extended nature.^{47,48}

2. 170–150 nm. From 170 to 150 nm, the optical absorptivity of benzene declines by about an order of magnitude in the vapor and by about a factor of 2.5 in the neat liquid.² The large majority of the oscillator strength in this region appears to be associated with the blue edge of the $S_0 \rightarrow S_3$ transition, although there may be small contributions from other transitions.⁴⁰

The recovery of the benzene fluorescence in the neat liquid continues essentially unabated to 150 nm (see Figures 6 and 8). However, as the benzene is diluted, the rate of recovery slows down. For example, in the 2.2 M solution, the recovery only continues to 170 nm in *n*-hexane (Figure 6) and 174 nm in isooctane (Figure 8). At these wavelengths, the fluorescence excitation spectrum reaches a maximum and then begins to decline again. Since the absorption of light by the saturated hydrocarbon solvents begins to intrude in this spectral region, it is important to determine to what extent this contributes to the observed decline. Unfortunately, we do not yet have reliable values for the absorption coefficients of either dilute benzene or any saturated hydrocarbon liquid below 170 nm at the pertinent spectral resolution of our fluorescence measurements to make quantitative corrections for the absorption. But reasonable estimates of such corrections for the case of *n*-hexane at 170 nm indicate there will remain, in this decline, a real effect intrinsic to the benzene.⁴⁹ This conclusion is supported by

observing that as the benzene concentration increases above 2 M, although the decline at 170 nm diminishes in magnitude, there still always remains in the vicinity of this wavelength, even in the neat liquid, a slight inflection of the fluorescence excitation spectrum (see Figure 6). Also, from Figure 10, we note that in *n*-perfluorohexane a decline is observed in the excitation spectrum beginning at 168 nm, albeit there is at this wavelength less than 0.05% absorption by the solvent.

It is our view, then, that, in very dilute solutions, were we able to adequately correct for solvent absorption, the benzene $S_1 \rightarrow S_0$ internal conversion efficiency would be found to decline from 170 nm to at least 166 nm in a continuation of the decline observed at longer wavelengths. Increasing the benzene concentration to 0.560 M and then to 2.24 M causes a halt in the decline and a recovery of the fluorescence in the vicinity of the maximum of the $S_0 \rightarrow S_3$ transition (as previously discussed) but fails to abort the decline to the blue of 170 nm. Only at higher concentrations, above 4.48 M, do we observe the dilute solution behavior to be totally thwarted, even below 170 nm, and the recovery of fluorescence to persist to at least 150 nm. Such behavior is not unexpected. If indeed the effect of increasing benzene concentration to cause recovery of fluorescence at 190 nm is due to the generation of collective states, then clearly its manifestation must require not only a high density of benzene molecules but, additionally, a high spectral density of oscillator strength.⁵⁰ Accordingly, we might anticipate that, in regions of lower oscillator strength density (such as exists between 170 and 150 nm), higher benzene concentrations would be required to excite the collective modes.

In the 0.560–2.24 M *n*-hexane solutions (see Figure 6), the decline in $\beta_f(\lambda)$ continues to ca. 162 nm (hereafter referred to as region 1), beyond which $\beta_f(\lambda)$ again begins to recover. This recovery persists from 162 to 155 nm (region 2), and then once again there is reversal and loss of fluorescence from 155 to 150 nm (region 3). These undulations, as we discuss briefly below, are simple consequences of electronic energy transfer from the *n*-hexane to benzene.

In regions 2 and 3, the excitation spectrum of benzene in the 0.560 to 2.24 M solutions in *n*-hexane is similar in appearance to the fluorescence excitation spectrum of *n*-hexane except for being shifted to the blue (see Figure 9). As was previously noted (see section III), benzene reduces the *n*-hexane emission both via "inner filter" and dynamic quenching effects. The "inner filter" operates most effectively on the red edge of the *n*-hexane absorption spectrum, leading to a shift of the neat *n*-hexane fluorescence excitation spectrum to the blue. Indeed, it was by an analysis of this shift for a 0.11 M solution that we were able to extract some information about the ratio of the benzene to hexane absorption coefficients.

If the dynamic quenching of the *n*-hexane results in the production of an excited benzene via energy transfer, we would expect that were the benzene concentration sufficiently high so as to intercept most of the excited *n*-hexane before it emits but not high enough to compete with *n*-hexane for absorption of light in region 3, the fluorescence excitation spectrum of the benzene in regions 2 and 3 would closely mimic the excitation spectrum of neat *n*-hexane. This is indeed what we observe except for the aforementioned blue shift due to the "inner filter" effect. Additionally, we have found that the intensity of the benzene fluorescence in region 3 follows approximately the Stern–Volmer form $Kc/(1 + Kc)$ in its dependence on benzene concentration, c . This was demonstrated by noting that, for all wavelengths from 147 to 157 nm and over a concentration range from 0.0090 to 0.22 M, the ratio R of the fluorescence intensity divided by $Kc/(1 + Kc)$ is independent of concentration for

arbitrary A and for $K = 10 \text{ M}^{-1}$. The constant K , which should be identified with the product of the *n*-hexane lifetime and the energy transfer rate constant,²⁴ is indeed not too disparate from what would be predicted using an *n*-hexane lifetime of ca. 0.3 ns^{51–54} and a diffusion-limited rate constant of $3 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.⁵⁵ For benzene concentrations above 0.22 M, the ratio R begins to increase with increasing benzene concentration due to increasingly important contributions to the benzene fluorescence from direct absorption of the exciting light.

In the case of isooctane, a similar procedure gives a constant value of R with $B = 0.02 \text{ M}^{-1}$ up to $c = 1.1 \text{ M}$. The ca. 500-fold reduction in B for isooctane vis-a-vis *n*-hexane is most likely contributed to mainly by a disparity in their excited state lifetimes. The absence of any reports of fluorescence from isooctane⁴² and estimates based thereon of a fluorescence quantum yield less than 5×10^{-6} are consistent with this view. The much larger range of concentrations over which the superposition is valid in isooctane as compared to hexane is due, most plausibly, to a significantly larger optical absorption coefficient of isooctane in this spectral region,⁵⁶ which shifts the intrusion by benzene absorption to higher concentrations.

Finally, it should be noted that the behavior of the excitation spectrum in the spectral region below 165 nm becomes even further complicated by the opening up at ca. 162 nm of still another channel to S_1 involving the ionization of benzene and recombination of the electron with the benzene cation.¹⁵

D. Effect of Chloroform. As was reviewed in section I, previous explanations for the minimum in the fluorescence excitation spectrum of neat liquid benzene at a wavelength close to the $S_0 \rightarrow S_3$ absorption maximum assumed the existence there of an ionization threshold.^{9,10,12} This was deduced from what appeared to be the onset at ca. 178 nm of a strong quenching action by chloroform acting as an electron scavenger. Since recent measurements of the ionization threshold of neat liquid benzene have suggested its location at $162 \pm 2 \text{ nm}$,¹⁵ we have sought other possible explanations for the action of chloroform.

Figure 11 shows the effect of 0.12–0.50 M chloroform on the fluorescence quantum yield of neat liquid benzene at various excitation energies.¹¹ The ordinate is the ratio of the benzene $S_1 \rightarrow S_0$ fluorescence intensity in the presence of the chloroform to that in its absence, and the magnitude of its downward deviation from unity is a measure of the strength of the quenching action. It will be noted from Figure 11 that as the chloroform concentration increases, strong discrete quenching actions develop in the regions around 222 and 177 nm, the latter of which is superimposed on a general background that increases from 205 to 150 nm.

The region around 222 nm is one of very weak absorption by both benzene and chloroform separately, but in their mixtures we have found an enhancement of absorption above that expected from their sum. This, of course, is the typical signature of contact charge transfer absorption or absorption by a stable complex. Accordingly, the quenching of fluorescence in the vicinity of 222 nm is, most plausibly, a consequence of an "inner filter" effect due to the absorption by a nonfluorescing chloroform–benzene entity. Similar perturbations by chloroform on the benzene $S_0 \rightarrow S_1$ absorption spectrum have been previously noted.⁵⁷ The rapid recovery of I/I_0 to the blue of 222 nm is attributable to the onset of the relatively intense $S_0 \rightarrow S_2$ absorption system and its favorable competition with the chloroform–benzene entity for light absorption.

The second region of enhanced quenching activity begins at 188 nm, rapidly declines to a minimum at 177 nm, and then recovers to the background level at 170 nm. Were the quenching here to derive from a scavenging of electrons

(preventing thereby their radiative recombination with benzene positive ions), it would be extremely difficult to understand why such a scavenging would first increase to 177 nm and then decline at shorter wavelengths. On the other hand, there is an obvious similarity between the 177 and 222 nm features that makes more plausible similar assignments as "inner filter" effects of a chloroform–benzene entity. Of course, for the 177 nm feature, it would be now the sharp red edge that would be explained by competition for light with benzene's intense $S_0 \rightarrow S_3$ transition. A more detailed study of the effects of the chloroform and other electron scavengers on the fluorescence action spectrum of benzene will be presented elsewhere.

E. Excimer–Monomer Equilibrium. From an analysis of excimer–monomer kinetics, it is simple to establish that the ratio of fluorescence intensity from excimer (E_0) to that from excited monomer (S_1) will be independent of whether monomer or excimer is excited directly, so long as the temperature is sufficiently high for (i) the dissociation reaction $E_0 \rightarrow S_0 + S_1$ to be large compared to all other decay channels of E_0 and (ii) the association reaction $S_1 + S_0 \rightarrow E_0$ to be large compared to all other decay channels of S_1 .²⁵ When either or both of these constraints disappear, the excimer to excited monomer fluorescence intensity ratio is expected to depend on the excitation process.

From reported data on the benzene dissociation and association constants,²⁵ it can be concluded that at 20 °C the aforementioned "equilibrium" conditions are *both* satisfied. Accordingly, we would not expect (nor did we find)²³ any change in the benzene emission spectrum with excitation energy. However, as the temperature is lowered (below ca. –30 to –40 °C), the excimer/monomer data on benzene²⁹ indicate that condition (i) becomes sufficiently violated for the emission spectrum to become now sensitive to whether excimer or monomer is formed directly.²⁹ Accordingly, if an excited excimer (E_1) were directly generated in the vicinity of the shoulder and decayed to S_1 via thermalized states of E_0 , then we should observe at these temperatures some increase in the excimer to monomer ratio of the emission spectrum for the higher energy excitations.

Neat liquid benzene freezes at 5 °C, which is too high a temperature for observation of changes in the excimer to monomer ratio. On the other hand, in preliminary experiments at 2.4 M benzene in hexane at –40 °C we observed no change in emission spectrum over all three excitation bands, despite the fact that the excimer to monomer intensity ratio increased 60-fold over that observed at 20 °C. Also, in preliminary experiments with neat toluene, no excitation energy dependence of the emission spectrum has been observed in studies from 20 to –100 °C. The implication of these results is that if indeed excited excimers are formed at the higher energies, they generate $S_1 + S_0$ either through direct dissociation or via nonthermalized levels of E_0 .

F. Surface Quenching at the Window–Liquid Interface. There is no question but that S_1 states of benzene are quenched at the window–liquid interface and that this causes the fluorescence excitation spectrum to be artificially depressed in spectral regions where the penetration depth of the exciting light is small.^{1,3,7,8} However, as we have attempted to demonstrate in previous sections, the effect cannot account for the important major features of the spectrum.

To quantify this, we utilize Feinleib's³ simple one-dimensional diffusional model for an excited S_1 state of benzene (with diffusion constant D) that decays unimolecularly with a rate constant s and is generated at a rate which decreases exponentially with distance from the window ($q \exp(-\alpha x)$). If we

further constrain the concentration c of S_1 to be zero at the window, it is then easily derived that in the steady state the total number N of S_1 states is given by $N = N_0/(1 + \kappa)$, where $\kappa = [\alpha^2 D/s]^{1/2}$ and N_0 is simply the value of N in the limit $\alpha \rightarrow 0$. Using for D the self-diffusion constant of benzene in the neat liquid ($D = 2.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)⁵⁸ and for s its S_1 decay constant ($s = 3.3 \times 10^7 \text{ s}^{-1}$)⁵⁹ and for α the absorption coefficients for neat liquid benzene^{2,16} for excitation at 254 nm ($\alpha = 2.5 \times 10^3 \text{ cm}^{-1}$) and at 190 nm ($\alpha = 2.7 \times 10^5 \text{ cm}^{-1}$), we obtain a value for $N(190)/N(254)$ of 0.82. Accordingly, we would expect that at 190 nm our fluorescence excitation spectrum should be upward corrected by about 22%.

When 0.014 M PPO is added, essentially all of S_1 is intercepted by PPO and $N(190)/N(254)$ is predicted from eq 3 to be 0.95 (using now $s = 7.2 \times 10^8 \text{ s}^{-1}$).⁶ This gives a correction to the fluorescence excitation spectrum when PPO is monitored of only 5%. Accordingly the ratio of the excitation spectra of PPO to that of benzene is expected to be ca. 1.2 at 190 nm. A similar calculation at 205 nm ($\alpha = 1.0 \times 10^5 \text{ cm}^{-1}$) gives for this ratio 1.0₂.

Figure 12A shows the fluorescence excitation spectra of neat liquid benzene and of 0.014 M PPO in the neat liquid. (Except for the region of the "shoulder", where absorption by PPO tends to obscure its presence, all other features of the benzene fluorescence excitation spectra are preserved in the spectrum of PPO. Figures 6c and d shows a similar comparison of the two fluorescence excitation spectra for a 2.2 M solution of benzene in the region from 190 to 150 nm. Again, we note that the broad undulations observed in the benzene fluorescence excitation spectrum (see section IV.C.2) are preserved in the PPO spectrum (albeit shifted upward)). The ratio of the two spectra in Figure 12B reproduces reasonably well the absorption spectrum of benzene from 170 to 190 nm not only in the positions of the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ systems but also in the relative absorptivities in these regions (when unity is subtracted from the ratio). However, the diffusion model provided above appears to somewhat underestimate the quenching at the interface. Thus, whereas the prediction for the ratio at 190 nm is 1.2, a value of 1.5 is observed (see Figure 12B) and, at 205 nm, the experimental ratio is 1.2 as compared to the predicted ratio of 1.0₂. The origin of the discrepancy is not known but may be attributable to contributions in the neat liquid from excitation diffusion to the window and from transient effects (ignored in our steady state solution) at the interface.

Replacing the LiF window with MgF₂ or even Suprasil quartz had very little effect on the fluorescence excitation spectrum. Accordingly, it may be not the window but rather a phase boundary that is responsible for the quenching effect. Preliminary measurements on microcrystalline toluene confirm this. Thus, entirely similar quenching effects are observed in the solid even in the absence of a window (presumably via energy migration to a vapor–solid phase boundary).

V. Conclusions

A. Dilute Solutions. In dilute solutions of benzene in saturated hydrocarbon solvents, the fluorescence quantum yield of benzene falls off monotonically with increasing excitation energy beginning at the onset of the $S_0 \rightarrow S_2$ (B_{1u}) system at 225 nm and extending to at least 166 nm, which lies on the short-wavelength side of the $S_0 \rightarrow S_3$ (E_{1u}) system. The rate of this falloff is maximal for transitions on the red edges of both of these systems, with the rate declining as the excitation energy sweeps to the blue and into the major part of the absorption systems. This falloff is attributed to essentially the same process that has been suggested to explain the development

of the so-called "channel 3" process in the vapor phase. At the edges of each absorption system, it is suggested that the dominating transitions are to "nonvertical"⁴³ vibronic states of the S_2 and S_3 surfaces that are distorted along some valence isomerization coordinate and couple strongly to S_0 . Indeed our use of such distorted states follows from the suggestion of Sobolewski that channel 3 in the vapor is due to an intersection of S_1 with S_2 and then its further intersection with S_0 along this distortion coordinate.³⁴

Perturbations provided by the saturated hydrocarbon solvent postpone the onset of channel 3 in the liquid by ca. 0.5 eV to the $S_0 \rightarrow S_2$ onset at 225 nm. However, in a more weakly perturbing perfluorocarbon solvent, the onset remains at its vapor value, suggesting that collisional broadening of the S_1 vibronic levels of benzene (which is much greater for the hydrocarbon solvents) is required to subvert the internal conversion at the S_1-S_2 intersection.

Even the hydrocarbon solvents, however, are unable to prevent the loss of fluorescence when these distorted states are directly excited on entrance into S_2 . The fluorescence continues to fall rapidly until the excitation energy sweeps above the 0-0 "vertical" origin of the $S_0 \rightarrow S_2$ transition and then slows down as vibronic states are generated at the saddle-point geometries of the S_2 surface and are assisted by the hydrocarbon solvents to make radiationless transitions to S_1 .

On entrance into S_3 , as on entrance into S_2 , the fluorescence excitation spectrum again is observed to sharply increase its rate of decline and again to eventually slow down in this rate of decline as the excitation energy sweeps into the major part of the absorption spectrum. Here too, these effects are attributed to a change in the position on the S_3 surface that is accessed at the long and shorter wavelengths of the absorption system.

This reduced rate of decline continues to about 166 nm. At shorter wavelengths, we have been unable to untangle contributions to the benzene fluorescence from direct absorption by the benzene and from energy transfer to benzene from the saturated hydrocarbons whose excitations begin to dominate in this spectral region. In the case of cyclohexane and *cis*-decalin, the parameters of this energy transfer agree well with earlier and more detailed studies by Johnston et al.^{21,30} In the case of *n*-hexane, whose energy transfer to benzene has not been previously studied, the parameters are consistent with a 0.3 ns lifetime of excited *n*-hexane, in good agreement with direct measurements of this time by Lyke.⁵² For isooctane, there appears also to be evidence for an energy transfer to benzene albeit with an efficiency ca. 500 times smaller than that from *n*-hexane. This is compatible with the Rothman et al.⁴² upper bound estimate of the isooctane fluorescence quantum yield *vis-a-vis* the fluorescence quantum yield of *n*-hexane.

B. Concentrated Solutions. As the benzene concentration increases, the fluorescence action spectrum changes by the appearance of discrete regions where the rate of decline of the fluorescence is temporarily abated or even reversed. The positions of these structures shift red as the benzene concentration increases in a manner consistent with the red-shift of the absorption spectrum. Numerous arguments are advanced that exclude the possibility of explaining these structures as artifactual.

The lowest energy structure occurs in the neat liquid as a very brief interval (from 217 to 213 nm) of a slow-down in the rate of decline of the fluorescence. It occurs at a spectral position very close to where anomalously high multiphoton ionization efficiencies of small vapor clusters of benzene have been reported by Shinohara and Nishi.⁴⁰ Their suggested explanation of direct excitation to an excited excimer state (or

a van der Waals precursor of this) of longer lifetime than would be excited at lower concentrations is adaptable to our data. Excited excimer states will decay efficiently to monomeric S_1 either directly or via the lowest excimer state (E_0). Since the emission spectrum shows, even at low temperatures, no change in the ratio of excimer to monomer contributions, it can be concluded that the decay of E_1 cannot utilize thermalized levels of E_0 . Also, it is concluded that the absorption coefficients of the excimer or pre-excimer states cannot be very large, since the fluorescence continues to decline rapidly as the $S_0 \rightarrow S_2$ absorption amplitude gains strength to the blue of the "shoulder".

The more prominent structures (first observed in neat liquid benzene by Kato et al.¹ and subsequently confirmed by many other workers)³⁻⁵ are plateaus that begin to develop with increasing concentration in the regions of major absorptivity of the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ absorption systems. In the case of the " S_3 plateau", as the concentration increases above ca. 1 M, the plateau develops into a minimum at a wavelength slightly to the blue of the $S_0 \rightarrow S_3$ absorption maximum. The fluorescence quantum yield thereafter begins to rise and continues to rise to 150 nm in the neat liquid and to ca. 170 nm in a 2 M solution of benzene in hexane. The recovery is considered to be due to the development of collective excitations in this region of very high electronic oscillator strength density. This view is consistent with dramatic changes that occur in the $S_0 \rightarrow S_3$ absorption system upon change in concentration. The collective states couple very efficiently to lower electronic states due to maintenance (by virtue of their spatial diffuseness) of the "vertical" equilibrium geometry of D_{6h} . These effects on the fluorescence excitation spectrum of the liquid in this spectral region also appear to be related to recent reports by Schriver, Hahn, and Whetten⁴⁶ of anomalously high ionization efficiencies of large benzene clusters excited at 193 nm in the vapor.

As the benzene differential oscillator strength declines in the shorter wavelength regions of the $S_0 \rightarrow S_3$ absorption system, the concentration of benzene in solutions less than ca. 4 M becomes inadequate to maintain the collective modes. The fluorescence excitation spectrum in these solutions reverses its slope and begins again to decline at ca. 170 nm. This decline continues to about 166 nm. At shorter wavelengths the effects of solvent absorption obscure the behavior of directly excited benzene. In solutions of higher concentration, however, the recovery persists to 150 nm. Part of this latter recovery is assisted by the opening up at 162 nm of ionization channels S_1 .

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