The Photoionization Spectrum of Liquid Benzene

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The Photoionization Spectrum of Liquid Benzene

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The photocurrent from neat liquid benzene has been studied for excitation energies from threshold to 10.3 eV and for externally applied electric fields from 1 to 50 kV/cm. Using a power law fit to the energy dependence of the threshold current, an onset of $\epsilon_t = 7.65 \pm 0.1$ eV has been obtained. The field dependence was fit to an exponential radial probability density for thermalized ion-pair separation distances with an average separation distance of $\langle r \rangle = 23 \pm 2$ Å at an excitation energy, ϵ, of 8.86 eV (1.2 eV above threshold). Photocurrent was too weak to establish a dependence of $\langle r \rangle$ on excitation energy. The quantum yield for photocurrent at 8.86 eV was determined by comparison with the photocurrent from TMPD in 2,2,4-trimethylpentane (isooctane) to be 6.5×10^{-4} at zero field. From this, the intrinsic molecular ionization probability at $\epsilon = 8.86$ eV was determined to be 0.6 ± 0.3.

I. Introduction

The ionization threshold of neat liquid benzene was first estimated by Fuchs and Voltz[1] and later by Schwarz and Mautner[2] to lie at ca. 7.0−7.1 eV. Their estimate was essentially based on what appeared to be an onset at this energy of a large increase in the quenching effect of chloroform on the fluorescence quantum yield of benzene. The suggestion was that at this energy the benzene fluorescence begins to derive, in part, from positive ion plus electron recombination and that chloroform acts to scavenge the electron and, thereby, inhibit this part of the fluorescence. Such an interpretation of the action of chloroform is not without some difficulty, and a critique is presented elsewhere.[3]

In 1982, Scott, Braun, and Albrecht[4] reported the observation of photocurrent from neat liquid benzene via two-photon excitation to a state at 7.4 eV. Assuming that the observed photocurrent was not due to direct generation of ion-pair states lying below the true threshold, they argued from an estimate of the polarization energy of the positive ion that, more plausibly, the true threshold lies ca. 0.3−0.4 eV below 7.4 eV which they noted would be consistent with the Fuchs and Voltz[1] and Schwarz and Mautner[2] estimates. For solid benzene, earlier work by Asaf and Steinberger[5] showed that photoemission at 90 K had a threshold of 7.58 eV. On the assumption that the cation polarization energy (P_+) is the same for solid as for liquid benzene, the difference between the "solid" photoemission and "liquid" photoionization thresholds would then reside entirely in the 0.14 eV "vertical" electron affinity of the liquid (i.e., $-V_0 = 0.14$ eV).[6] This would place the liquid threshold at 7.44 eV, or even somewhat larger, if P_+ (solid) exceeds P_+ (liquid) due to the larger density of the solid.

In this paper we report on direct one-photon measurements of photocurrent from neat liquid benzene for excitation energies from threshold to 10.3 eV. The dependence of the photocurrent on the magnitude of an externally applied electric field is also reported and compared with the data for N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) in 2,2,4-trimethylpentane. From this, we have estimated both the range parameter of the ejected electron in neat liquid benzene and the intrinsic quantum yield for photoionization.

II. Experimental Section

A Hamamatsu L879 30-W D_2 discharge lamp (fitted with a MgF_2 window) was used to cover the desired photon energy range. The exciting light was passed through an Acton VM502 (0.2 m) monochromator operated at a band pass of 1 nm and flushed with N_2. Light emerging from the monochromator was focused on the front surface of the cell by a parabolic mirror.

A stainless steel photoconductivity cell was used for measurements of the wavelength dependence of photocurrent in the VUV region. Light entered through a 0.1 cm thick LiF window of active diameter 2.54 cm and was focused in a spot of size approximately 0.05×1 cm^2. Photocurrent was collected by a pair of stainless steel rectangular 2.2 cm $\times$ 1.27 cm electrodes spaced 0.084 cm apart. To reduce the magnitude of the noise, the electrodes were polished to optical flatness. Electrodes were attached to a Ceramiseal connector soldered to a flange and assembled to a body through an indium O-ring. One of the electrodes was spring-loaded and insulated against the cell body by a Macor ring. The other electrode was rigidly mounted. Spacing was obtained by insertion of a quartz spacer between the electrodes. Dark dc level was reduced by applying an electric field of about 50 kV/cm for a prior period of at least 24 h.

A cell with a front semitransparent (Ta-film) photocathode was also used for studies above 10 kV/cm and above 150 nm (at which wavelength the optical transmission of the photocathode window became too small for reliable measurement.[7,8] In this regime, the results obtained with this cell and with the aforementioned cell were in good agreement except for a small, ca. 5%, discrepancy at the highest field strengths. At fields below 10 kV/cm, image charge effects were observed with the semitransparent electrode very similar to what has previously been reported by Bottcher and Schmidt.[9]

The photocurrent was measured with a Keithley 602 electrometer. The dc-signal from the electrometer was converted to digital form by a Data Translation DT2801 board in conjunction with an IBM-PC computer. A BASIC program was used to store and manipulate the data obtained.

To obtain a photocurrent spectrum, the measured electrometer signal was corrected both for the wavelength dependence of the lamp intensity and for contributions from dark current. The intensity of the D_2 lamp was measured in the spectral region

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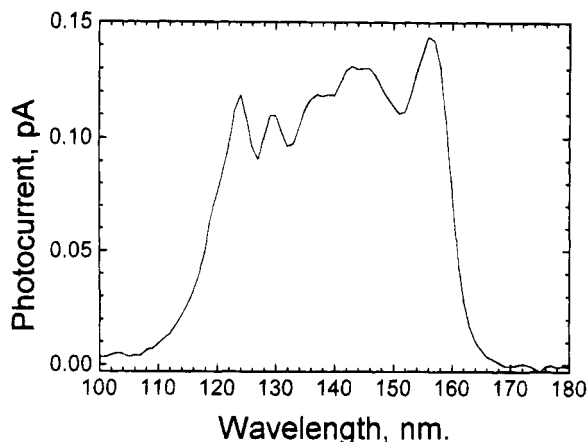
Figure 1. Photocurrent from liquid benzene as a function of excitation wavelength at an electric field strength of 24 kV/cm.

Figure 2. Spectral distribution of the lamp as determined by the relative intensity of the fluorescence of *cis*-decalin.

120–180 nm by measuring the fluorescence intensity from neat *cis*-decalin placed in the same photoconductivity cell. As has been demonstrated elsewhere, *cis*-decalin has a constant fluorescence quantum yield in this region of excitation energies.[10] At lower energies, the lamp intensity was monitored by the use of a solution of 10^{-2} M 2,5-diphenyloxazole (PPO) in n-hexane. In all fluorescence measurements, the emission was collected from the cell front surface by a Suprasil quartz lens and dispersed through a McPherson 218 (0.3 m) monochromator operating at a band pass of 5.4 nm. The dispersed light was made incident on a Hamamatsu R943-02 thermoelectrically cooled photomultiplier from which single photon pulses were individually counted.

Benzene (OmniSolv, glass distilled or Fisher, Spectranalyzed) samples were always additionally purified. The procedure that provided samples with the lowest dark current utilized a distillation of the benzene (three to five times) with an adiabatic Teflon spinning band distillation column (Nester/Faust) operating at a reflux ratio of 20:1. This was followed by stirring with a molecular sieve (pore size, 4 Å) for at least 24 h. The sample was then recrystallized at 0 °C under vacuum and, finally, restirred with molecular sieve for another 24 h. Treated in this way, the resulting benzene had a dark current of only ca. 2 pA at a field strength of 30 kV/cm (i.e., a resistivity of about 2 × 10^{16} Ω·cm). During storage of the samples, dark current was observed to increase, so only freshly prepared samples were used in all measurements.

Cis-decalin (Aldrich, 99%), cyclohexane (Mallinckrodt, spectrophotometric grade), 2,2,4-trimethylpentane (Aldrich, 99%, spectrophotometric grade), and hexane (OmniSolv, glass distilled) were additionally purified by passage through a column containing activated silica gel. PPO (Aldrich, scintillation grade) was used without further purification. TMPD (Aldrich, 98%) was sublimated in vacuum. All solutions were deoxygenated by bubbling with N_2 and all measurements were made at 22 °C.

III. Results

A typical photocurrent spectrum of liquid benzene is shown in Figure 1. A rather large but stable dark current background at 2 pA has been subtracted from the spectrum, but it is not yet corrected for the spectral distribution of the lamp. The lamp spectrum is shown in Figure 2 as determined from the fluorescence intensity of *cis*-decalin (placed in the same cell). The ratio of solution photocurrent to lamp intensity is exhibited in Figure 3 from 120 to 180 nm. Below 120 nm, the lamp intensity was considered too weak for reliable measurement.
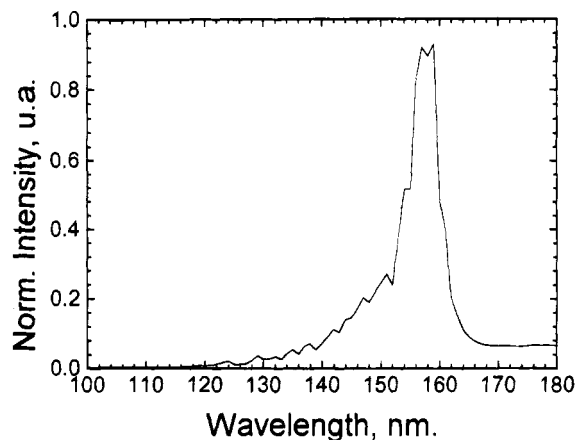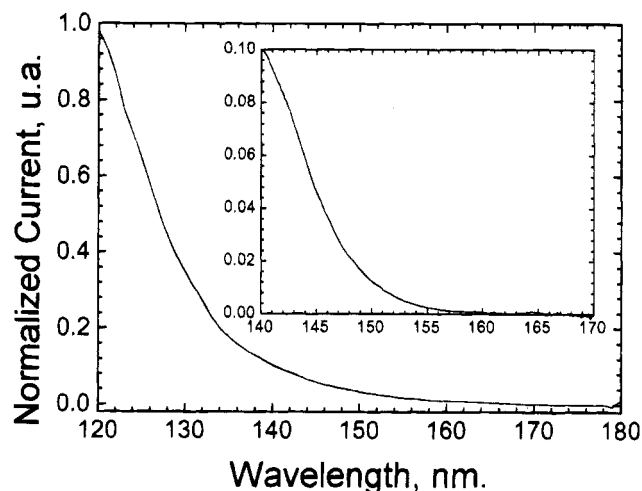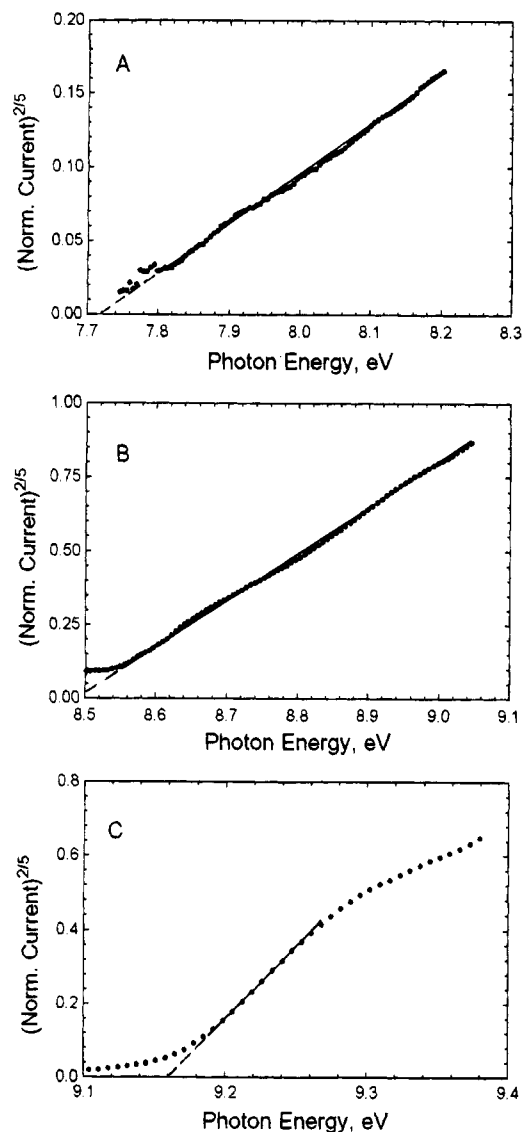

Figure 3. Photocurrent spectrum of liquid benzene corrected for the spectral distribution of the lamp. The spectrum shown as an insert was a separate experiment made with 10× greater current sensitivity and digital conversion rate.

As is apparent from Figure 3, the determination of a threshold of photoionization is made ambiguous by the slow decline of current above 160 nm. This problem is manifested also in measurements of photocurrent thresholds of neat saturated hydrocarbon liquids[11,12] albeit somewhat less pronounced than in benzene. The long tail is, in part, contributed to by impurity ionization and to some extent by "hot" transitions but is, most plausibly, mainly due to "direct" transitions to ion-pair states that lie below the threshold.[4]

The usual procedure for extracting a threshold is to seek a function that linearizes the photocurrent J, on the difference between the excitation energy, ϵ, and the threshold value ϵ_t. The function that seems to work best in this regard is $(\epsilon - \epsilon_t)^{5/2}$.[11,12] Figure 4a shows some of our results for neat liquid benzene as a plot of $J^{2/5}$ vs ϵ. For comparison, we also plot in Figure 4b and c data that we have obtained for neat liquid cyclohexane and for 10 Torr of benzene vapor, respectively. For cyclohexane, we obtain a threshold of 8.5 eV which is in good agreement with earlier values of 8.43 ± 0.05 eV[11] and 8.45 eV.[13] For benzene vapor, our value of 9.1_5 eV is to be compared with a previous photocurrent threshold value of 9.2 eV[14] and with a vertical ionization potential of 9.25 eV.[15] In the case of neat liquid benzene, the data shown in Figure 4a are typical of what was obtained from eight other samples and averaging over all of these gives a threshold energy of 7.6_5 ± 0.1 eV.

Figure 4. Corrected photocurrent spectra shown as a plot of $J^{2/5}$ vs excitation energy ϵ for (a) liquid benzene, (b) liquid cyclohexane, and (c) 10 Torr of benzene vapor.

The dependence of the photocurrent on the magnitude of an externally applied electric field is shown in Figure 5a for neat liquid benzene for excitation at 140 and 156 nm. For the purpose of estimating a photocurrent quantum yield, TMPD at a concentration of 2×10^{-3} M in isooctane was examined in the same cell for excitation at 215 nm. The TMPD results are shown in Figure 5b.

IV. Discussion

For a variety of saturated hydrocarbon liquids, either neat or with aromatic solutes, there appears to be a reasonably well-defined excitation energy above which photocurrent rapidly increases[11,16,17] in a manner not too dissimilar (albeit slower) from what is observed in the gas phase. This result is initially surprising when one considers that unlike the gas, where there is essentially no ionization below the ionization potential, ϵ_g, (neglecting "hot" transitions and AB $\rightarrow$ A + B$^+$ + e$^-$ dissociative transitions), in the liquid phase there must exist a continuum of ion-pair states with energy below the liquid ionization threshold ϵ_t ($= \epsilon_g + P_+ + V_0$).[18] However, large radius ion-pair states which could contribute to photocurrent by virtue of their large escape probabilities must be difficult to access either via direct optical transition or via indirect nonra-
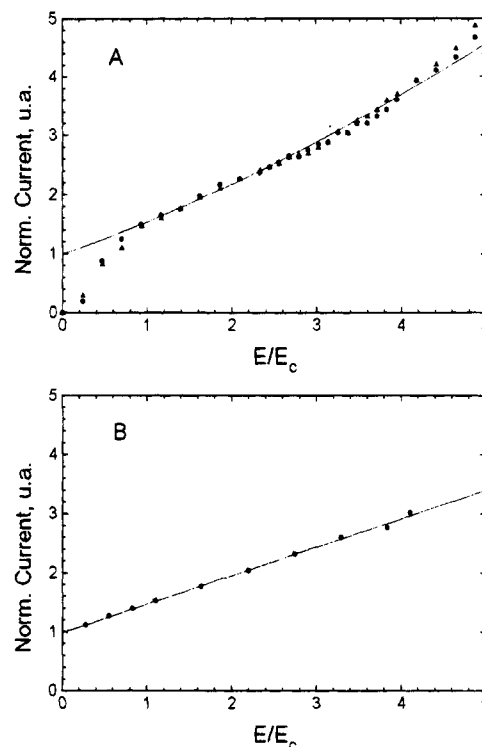
Figure 5. Dependence on the electric field strength of the photocurrent signal of (a) neat liquid benzene (E_c = 10.1 kV/cm) at two excitation wavelengths (●) 140 nm and (▲) 156 nm and (b) a solution of 2 × 10^{-3} M TMPD in isooctane (E_c = 8.6 kV/cm) at an excitation wavelength of 215 nm.

diative transitions from the valence excited states, and the smaller radius ion-pair states, which could readily be accessed via both the direct and indirect transitions, are, most plausibly, too small for any appreciable escape. Accordingly there persists, even in these liquids, a remarkably sharp photocurrent onset but with a somewhat more pronounced low-energy tail.

To experimentally determine ϵ_t, it has been customary to fit some power of the observed photocurrent (i.e., J^p) to a linear regression on ϵ in the vicinity of the onset (i.e., within a few tenths of an electronvolt) and to interpret the extrapolated intercept at $J^p = 0$ as ϵ_t. Considering how complex is the origin of photocurrent in a liquid (due to its dependence on both the molecular ionization probability, $\Phi_\pm$, and the escape probability, P_{esc}), it is surprising to find that so simple a dependence of J on ϵ is adequate. Nevertheless, using $p = 2/5$, a variety of studies have obtained what are considered to be reasonable values of ϵ_t.[17-20] This reasonableness has generally been established in one of two ways. The first is by comparison with values obtained by independent techniques, such as the determination of the onset of chemical[21] or electric field quenching of recombination fluorescence,[13,22,23] the onset of magnetic field induced enhancement of recombination fluorescence,[24] or of positions of minima in the fluorescence action spectra of selected neat hydrocarbon liquids.[10] Unfortunately, however, the sensitivity of all of these other techniques in the location of ϵ_t is so much less than that of the photocurrent technique that only very qualitative comparisons have been possible.

The second basis for reasonableness has been to utilize the theoretical definition of ϵ_t as $\epsilon_g + P_+ + V_0$ and, with independently measured values of ϵ_g and V_0, to deduce therefrom a value for P_+ and then to compare this either with theoretical expectations or with experimental values deduced from photoemission measurements. For a variety of aromatic solutes dissolved in nonpolar hydrocarbon liquids, values of $P_+ = -0.9$

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to -1.2 eV have been deduced from the $J^{2/5}$ vs ϵ plots.[25] These values, when compared with predictions of the Born equation using an ion radius obtained from molecular densities, appear to be generally too negative by 20%.[17]

In the case of neat liquid benzene, the value of ϵ_t that we deduce from the $J^{2/5}$ extrapolation is $7.6_5 \pm 0.1$ eV. Although this is considerably above that of previous estimates of 7.0–7.1 eV (see section I), some support for its validity derives from the following considerations. First of all, we find from $\epsilon_g = 9.2$ eV and $V_0 = -0.14$ eV that $P_+ \approx -1.4$ eV. This differs from the value of -1.2 eV computed from the Born equation (using a molecular radius deduced from the molecular density) by ca. 17%, a value not too disparate from the discrepancy obtained for many other aromatics.[17] Second, from the photoemission threshold value of 7.58 eV for the 90 K solid,[5] a P_+ of -1.60 eV is evaluated. If we assume that P_+ scales with increasing density via reduction in the equivalent ion radius and via increase in refractive index, then by the use of the 0 °C solid density of 0.900 g/cm, we estimate that $|P_+|$ for liquid benzene should be decreased from the 1.60 eV value by at least 4–5%. Accordingly, the solid benzene photoemission value leads us to a predict a liquid $\epsilon_t = 7.5$ eV which lies within the uncertainty of our extrapolated value. Finally, as will be commented on elsewhere,[3] there exist features in the fluorescence action spectrum of liquid benzene which support a value close to 7.6 eV.

We next turn our attention to the field dependence of the photocurrent for both neat liquid benzene and for TMPD in isooctane. The abscissa in Figure 5 is the field strength in units of the Onsager critical field E_c, defined as $E_c = \epsilon k^2 T^2/e^3$, where ϵ is the dielectric constant of the solvent.[26] For neat benzene and for isooctane at 20 °C, $E_c = 10.1$ and 8.6 kV/cm, respectively. In the limit $E/E_c \rightarrow 0$, Onsager theory predicts that for an isolated ion pair, the photocurrent should approach linearity on E/E_c with a slope of 0.5.[8] In the case of neat liquid benzene, the observed fall off in photocurrent that begins at ca. $E/E_c = 1$ is attributed to homogeneous recombination of ion pairs. Its appearance at a higher field strength for neat benzene than for TMPD in isooctane is not unexpected in view of the much smaller penetration depth of the exciting light in benzene and concomitant higher concentration of ion pairs. However, from $E/E_c \simeq 1$ to $E/E_c \simeq 2$, the slope in Figure 5A is, within our experimental uncertainty, equal to the Onsager limiting slope of 0.5 implying that for $E/E_c > 1$, homogeneous recombination has become negligible.

The deviation from the Onsager limiting slope of 0.5 at higher field strengths is due to the effect of the field to increase the ion-pair escape probability and contains information about the radial probability density, $f(r)$, for ion-pair separation distances.[8] As has been found in other photoionization studies,[8,25] a reasonable fit to the field dependence of the photocurrent in this regime can be obtained from Onsager theory using an exponential probability density, i.e.,

$$f(r) = \left(\frac{\alpha^3}{2}\right) \exp(-\alpha r) \qquad (1)$$

Unfortunately, the weakness of the photocurrent signal in benzene did not permit us to reliably separate effects at the two excitation wavelengths of 140 and 156 nm. Accordingly, the fit shown as a solid line in Figure 5A is to the data for both excitation wavelengths using a value of $\alpha r_C = 33 \pm 5$, where r_c, the Onsager radius, $(r_c = e^2/(\epsilon kT))$ equals 250 Å for neat liquid benzene at 20 °C. For the exponential radial density, the average separation distance, $<r>$, equals $3/\alpha$ or ≈ 23 Å. For comparison, we note that for TMPD or anthracene in

isooctane $<r> \approx 70$–80 Å[27] and for neat cyclohexane $\langle r \rangle \approx 100$ Å at comparable energies above the threshold. This small average distance for benzene is consistent with our inability (and that reported by others as well[13]) to observe an electric field induced quenching of recombination fluorescence in neat benzene.

The photocurrent quantum yield, Φ_j, of neat liquid benzene at 140 nm was determined to be 6.5×10^{-4} by comparison of the photocurrent from benzene at 140 nm with that from TMPD in isooctane at 215 nm, both extrapolated to $E/E_c = 0$ via the Onsager limiting slope of 0.5, and using Choi and Braun's absolute value for the TMPD photocurrent quantum yield in isooctane.[8] The photoionization quantum yield, $\Phi_\pm$, of neat liquid benzene is obtained via

$$\Phi_\pm = \left(\frac{8\Phi_j}{\beta^3}\right) K_3^{-1}(\beta) \qquad (2)$$

where $\beta = 2(\alpha r_c)^{1/2}$ and $K_3(\beta)$ is the modified Bessel function of order 3.[27] Substitution of $\Phi_j = 6.5 \times 10^{-4}$ and $\alpha r_c = 33 \pm 5$ gives finally $\Phi_\pm = 0.6 \pm 0.3$.

A value of $\Phi_\pm$ of 0.6 is consistent with ionization probabilities obtained for neat saturated hydrocarbon liquids and also for other aromatics dissolved in these liquids at comparable energies above threshold. On the other hand, the much smaller average range of the electron in neat liquid benzene as compared to saturated hydrocarbons[28,29] suggests an anomalously efficient mechanism for electron thermalization and localization in the aromatic. Reversible electron attachment to benzene could provide such a mechanism were the cross section for epithermal electron capture sufficiently large and were the lifetime of transient negative ion sufficiently long for its decay to a lower energy electron. Although such data is unavailable, it is perhaps pertinent to note that studies of the pressure dependence of the mobility of the electron in neat liquid benzene by Itoh and Holroyd[30] have demonstrated that, at least in the equilibrium liquid, at 1 atm and 25 °C, the ratio of benzene anions to quasi-free electrons is 0.9.

V. Conclusions

From photocurrent measurements, an ionization threshold of $\epsilon_t = 7.6_5 \pm 0.1$ eV has been obtained for neat liquid benzene. This threshold value is 0.6 eV above previous estimates but is consistent with a photoemission threshold of solid benzene and with Born estimates of the positive ion polarization energy. The photocurrent quantum yield at zero applied electric field remains very low even at excitation energies 1.2 eV above threshold. Analysis of the field dependence of the photocurrent indicates that the low yield is due to a very small escape probability caused by an average thermal ion-pair separation distance of only 23 Å. The intrinsic ionization probability is, however, comparable to that of other aromatics that have been studied at comparable energies above threshold. The very small range of the ejected electron in neat benzene suggests an unusually efficient mechanism of rapid localization that is absent in saturated hydrocarbon liquids.

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