

# Luminescence Emission and Excitation Spectra of Benzene Thin Film under Slow Electron Impact at 77 K

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Luminescence bands of thin-film benzene at 77 K, excited by slow electron impact, are attributed to fluorescence of the monomer at 280 nm, and tentatively to fluorescence and phosphorescence of benzene isomers at 303 and 395 nm, respectively. The electron impact excitation spectra  $dL/dV_i$  vs.  $eV_i$  for the 280-nm band were measured, where  $L$  is the luminescence intensity and  $eV_i$  is the electron energy. Four peaks are clearly resolved which served for the calibration of electron energy, and thus for the assignment of peaks in the electron transmission spectra.

## Introduction

Recently Hiraoka and Hamill<sup>1</sup> and Sanche<sup>2</sup> reported a simple method for measuring the electronic levels of molecules supported as ultrathin films on a metal surface at low temperatures. The films were bombarded by a beam of low-energy electrons, and the current transmitted through the film ( $I_t$ ) was measured as a function of the incident electron energy ( $eV_i$ ). The electron transmission spectra, displayed as  $dI_t/dV_i$  vs.  $eV_i$  or  $d^2I_t/dV_i^2$  vs.  $eV_i$ , were found to be particularly useful for detecting optically forbidden electronic transitions. In our previous papers,<sup>1</sup> we calibrated the electron energy scale of the transmission spectrum for benzene by comparing it with the energy-loss spectra which were measured by the same apparatus. The energies of peaks in the transmission spectrum for benzene were in good agreement with those of electronic excited levels determined by the trapped-electron spectra<sup>3</sup> or energy-loss spectra<sup>4</sup> measured in the gas phase. With this electron energy calibration, the electron energy of the transmission spectrum should be shifted upward by 0.3 eV for correlation with that under vacuum. By the amount of this energy shift, the lowest conduction band energy  $V_0$  for solid benzene could be determined to be -0.3 eV.<sup>5,6</sup> This value is in good agreement with the  $V_0$  value of -0.14 eV obtained for liquid benzene.<sup>7,8</sup> On the other hand, by comparing the energies of peaks in the transmission spectra  $d^2I_t/dV_i^2$  vs.  $eV_i$  with those of electronic excited levels measured in the gas phase, Sanche concluded that the energy scale of the transmission spectra should be increased by 2.25 eV in order to establish a coincidence between structures present in both spectra.<sup>2</sup> Such a large discrepancy in the determination of the electron energy scale between these two groups cannot be reconciled and we decided to obtain the "absolute" electron energy scale by measuring the electron impact excitation spectra for luminescence for thin-film solid benzene.

## Experimental Section

The experimental procedures have been described previously.<sup>1,5</sup> Films were  $\sim 10$  monolayers thick. The electron current to the film was  $\sim 10^{-9}$  A for measurements of electron transmission spectra,  $\sim 10^{-7}$  A for luminescence emission spectra, and  $5 \times 10^{-8}$  A for luminescence excitation spectra. A Bausch and Lomb high-intensity monochromator was used for measuring emission spectra and a narrow band-pass filter was used for excitation spectra for benzene with  $\lambda_{\max}$  (and half-width) at 280 (20) nm. A Hamamatsu TV C1230 photon counter equipped with a Hamamatsu TV R585 photomultiplier was used for all measurements. The excitation spectra are presented at  $dL/dV_i$  vs.  $eV_i$  where  $L$  is the luminescence intensity and  $eV_i$  is the incident electron energy. Electron transmission spectra are presented as  $dI_t/dV_i$  vs.  $eV_i$  where  $I_t$  is the transmitted electron current through the film.

## Results and Discussion

**Emission Spectra of Solid Benzene.** The emission spectra of thin-film benzene at 77 K and several incident electron energies appear in Figure 1. The intensities were measured at intervals of 10 nm. At an electron energy of 8 eV (a in Figure 1), only the benzene fluorescence at 280 nm was observed. At  $\sim 13$  eV, new bands at 303 and 395 nm appeared and these new bands grew strongly as the electron energy was increased as shown in Figure 1. At 48 eV, the benzene fluorescence appears as only a shoulder peak on the 303-nm band. Spectrum f in Figure 1 was measured after the measurements of spectra a-e at the electron energy of 8 eV. The bands at 303 and 395 nm, which were absent in spectrum a, have persisted. These results suggest that the emitters of these bands are radiation products produced in the benzene film.

Phillips and Schug<sup>9</sup> observed the broad bands at  $\sim 300$  and  $\sim 400$  nm under the stimulation of solid benzene by 1-MeV electrons. They assigned these bands as the singlet, triplet, and their excimer emissions. We consider that the assignment of the broad 400-nm band as triplet and triplet excimer emissions is dubious because the observation of emission from the triplet states in pure organic crystals has been unsuccessful due to the triplet excitation migration and the rapid triplet-triplet annihilation.

The decay of 395-nm emission was recorded by setting the band-pass filter with  $\lambda_{\max}$  (half-width) of 390 (100) nm. The lifetime could be roughly estimated to be  $\sim 0.2$  s. It is likely that the 395-nm emission is the phosphorescence of the radiation products.

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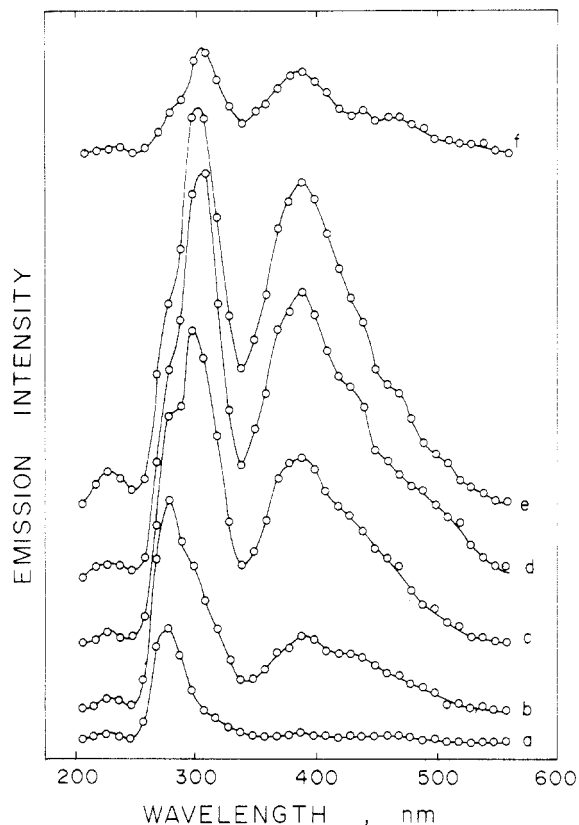
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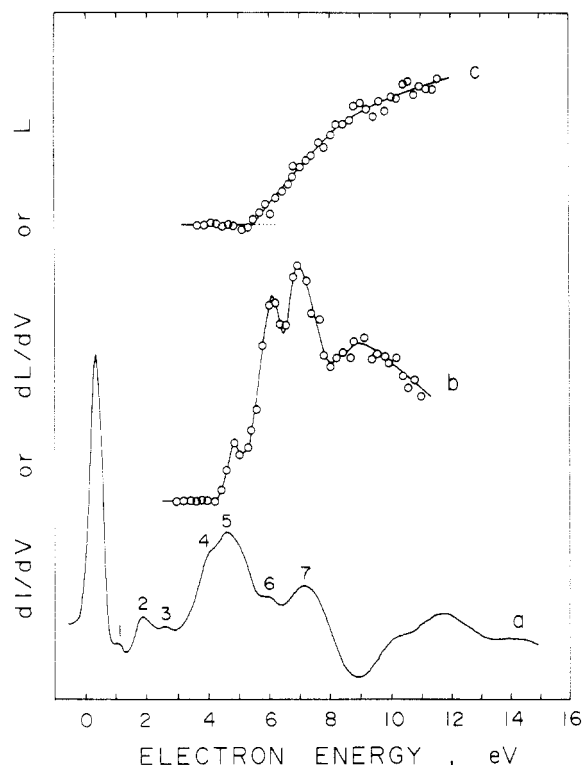


**Figure 1.** Emission spectra for thin-film benzene at 80 K under slow electron impact at (a) 8, (b) 13, (c) 18, (d) 23, and (e) 48 eV. Spectrum f was measured at 8 eV after the measurements of a–e. The film thickness was 10 langmuir. The incident electron current was  $\sim 10^{-7}$  A and the size of the electron beam spot was about 13 mm in diameter; i.e., the current density was  $\sim 10^{-7}$  A/cm<sup>2</sup>. Each point represents the relative intensity of photon counts accumulated for 10 s.

The 303-nm band can be attributed to neither the singlet benzene excimer emission nor the fluorescence of biphenyl, which is known as one of the major radiation products from benzene, because  $\lambda_{\text{max}}$  of these emissions are about 320 nm.

Many studies have been made on the vacuum-ultraviolet photochemistry of benzene.<sup>10</sup> Benzene irradiated by ultraviolet radiation in the gas and liquid phases is known to undergo isomerization to benzene isomers, mainly benzvalene and fulvene.<sup>11</sup> Although no luminescence of these benzene isomers has been reported, we propose that the 303- and the 395-nm bands are fluorescence and phosphorescence of some benzene isomer produced in the benzene matrix.

**Electron Impact Excitation Spectra for Solid Benzene.** In Figure 2 are shown the electron transmission spectrum,  $dI_t/dV_i$  vs.  $eV_i$ , and the electron impact excitation spectrum for luminescence,  $dL/dV_i$  vs.  $eV_i$ , for benzene. In our previous papers,<sup>1,5,6</sup> peaks 4 and 5 in the transmission spectrum were assigned to electronic excitations of  $^1A_{1g} \rightarrow ^3B_{1u}$  and  $^1A_{1g} \rightarrow ^1B_{2u}$ , respectively. However, Sanche<sup>2</sup> assigned peaks 2 and 3 to these electronic excitations. The calibration of the energy scale is one of the most important procedures in electron impact spectroscopy, and such a large discrepancy in the determination of the energy scale between these two groups is serious because they are using essentially the same techniques. As an alternative method to establish the zero of the energy scale, the electron impact excitation spectra for 280-nm fluorescence of benzene were



**Figure 2.** Electron transmission spectrum  $dI_t/dV_i$  vs.  $eV_i$  (a), the electron impact excitation spectrum  $dL/dV_i$  vs.  $eV_i$  for the 280-nm band (b), and the electron impact excitation spectrum  $L$  vs.  $eV_i$  for the 233-nm band (c) for 10 langmuir thick benzene film.

measured. As shown in Figure 2b, the luminescence has the onset at  $\sim 4.2$  eV and the excitation spectrum  $dL/dV_i$  vs.  $eV_i$  has four maxima at 4.8, 6.1, 7.0, and  $\sim 9$  eV. The energies of these peaks correspond closely to those of peaks 5–7 in the electron transmission spectrum. Since the emitting state is  $^1B_{2u}$ , peak 5 can be assigned to the  $^1B_{2u}$  excitation, indicating that the energy calibration of our previous papers is correct.

The peak at 6.1 eV in the excitation spectrum may be due to the cascade of  $^1B_{1u}$  state to  $^1B_{2u}$  state, followed by the radiative decay of  $^1B_{2u}$ . Hasnain et al.<sup>12</sup> measured the photon impact luminescence excitation spectrum of a benzene-doped krypton crystal. They observed sharp peaks which are due to the excitation of  $^1A_{1g} \rightarrow ^1B_{2u}$  and  $^1A_{1g} \rightarrow ^1B_{1u}$ . Since the emitting state is  $^1B_{2u}$  and  $^3B_{1u}$ , the observation of the luminescence in the energy region of the  $^1A_{1g} \rightarrow ^1B_{1u}$  excitation verifies the occurrence of an internal conversion from  $^1B_{1u}$  to  $^1B_{2u}$  state in the solid phase. However, they did not observe any peak in the energy region of  $^1A_{1g} \rightarrow ^1E_{1u}$  excitation. This result suggests that the cascade from  $^1E_{1u}$  to  $^1B_{2u}$  by an internal conversion is negligible. In the excitation spectrum shown in Figure 2, however, a rather sharp peak appears in the energy region of  $^1A_{1g} \rightarrow ^1E_{1u}$  excitation at  $\sim 7$  eV. If the cascade from  $^1E_{1u}$  to  $^1B_{2u}$  is negligible, this peak should not be due to emission of the  $^1B_{2u}$  state. It should be noted that the half-width of the band-pass filter used for the measurement of the excitation spectra was not narrow enough to cut off the emission of the 303-nm band. As the energy transfer from  $^1E_{1u}$  to the energy acceptor is known to occur in benzene solution,<sup>13</sup> the third peak at  $\sim 7$  eV in Figure 2 may be due to energy transfer from the  $^1E_{1u}$  state (i.e., excitons) to the radiation products, possibly some benzene

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isomer as discussed previously, followed by the radiative decay of the energy acceptor.

Fuchs et al.<sup>14</sup> measured the vacuum-ultraviolet excited fluorescence and concluded that the upper singlet levels in liquid benzene essentially decay by autoionization when their excitation energy is larger than a characteristic critical value of 7 eV. They observed efficient recombination luminescence which indicates that charge separation is followed by geminate recombination, without spin relaxation, from the lowest charge-transfer state to the  $S_1$  state. It is worthwhile noting that the broad fourth peak at  $\sim 9$  eV in the excitation spectrum is the mirror image of the large negative peak with the minimum at  $\sim 9$  eV in the transmission spectrum. Because the large negative peaks in the transmission spectra result from the ionization of molecules in the films,<sup>6</sup> the fourth peak in the excitation spectrum may be attributed to the recombination fluorescence.

It is noteworthy that the profile of the luminescence excitation spectrum shown in Figure 2 is very similar to the trapped-electron spectrum for benzene measured in the gas phase.<sup>3</sup> In other words, the peak intensities in the luminescence excitation spectrum roughly correspond to the relative cross sections for the resonant electron impact excitations for levels of  $^1B_{2u}$ ,  $^1B_{1u}$  ( $^1E_{2g}$ ), and  $^1E_{1u}$ . On the contrary, as shown in Figure 2, there is a marked difference in the relative peak intensities between the luminescence excitation spectrum and the electron transmission spectrum. The most characteristic difference is the large intensity of peak 5 in the electron transmission spectrum. Although peak 5 is attributed to the electronic excitation of  $^1A_{1g} \rightarrow ^1B_{2u}$  as mentioned previously, there seem to be some other contributions to this peak. The large peak in the electron transmission spectra  $dI_t/dV_i$  vs.  $eV_i$  corresponds to the sharp increase in the transmitted electron current through the film. In our previous papers,<sup>6,15</sup> it was suggested that the profile of the conduction bands must be reflected in the transmission spectra to some extent and

the peaks might correspond to the rising parts of the high density-of-states conduction bands.<sup>15</sup> In principle, any kind of vacant orbitals of free molecules can be candidates for the formation of the unoccupied conduction bands when molecules are condensed and form a molecular crystal. Jordan and Burrow studied the temporary anion states of unsaturated hydrocarbons in the gas phase by electron transmission spectroscopy.<sup>16</sup> They observed the vertical temporary anion states of benzene at 1.15 and 4.85 eV. In the electron transmission spectrum of benzene (Figure 2), a small but sharp peak 1 and a large peak 5 are observed at 1.2 and 4.8 eV. Such a good agreement suggests that peaks 1 and 5 correspond to the rising part of the high density-of-states conduction bands which are formed by these vacant molecular orbitals of benzene. The large intensity of peak 5 is likely to be due to the strong overlap of vacant molecular orbitals which makes the interaction between these orbitals strong, and high density-of-states conduction bands can be formed in the solid phase. A further investigation in this respect is now in progress in our laboratory.

In addition to the bands at 280, 303, and 395 nm, a weak band at 233 nm appears in Figure 1. In order to characterize this band, the electron impact excitation spectrum for this emission,  $L$  vs.  $eV_i$ , was measured by using a sharp cutoff band-pass filter with  $\lambda_{\max}$  (half-width) of 210 (30) nm. As shown in Figure 1c, the onset of the excitation spectrum corresponds to that of peak 6 ( $S_0 \rightarrow S_2$  transition) in the electron transmission spectrum. This suggests that the 233-nm band is due to the  $S_2 \rightarrow S_0$  fluorescence. Lipsky et al. observed the  $S_2 \rightarrow S_0$  fluorescence of benzene at 230 nm in the vapor and neat liquid phases.<sup>17,18</sup> The location of the weak band observed in this experiment also argues for  $S_2$  fluorescence assignment.

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## Free-Radical Concentration in Doped Sulfur. Theory and Experiment

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We present here a comparison between theory and some recent measurements of the ESR spectrum of liquid sulfur doped with various impurities. The data are taken near the polymerization transition temperature of pure sulfur and are interpreted as a measure of the concentration of the radical chain ends. By means of a simple equilibrium theory of Tobolsky-Eisenberg (TE) type we explain the observed signal intensity of the doped samples, which coincides with that of pure sulfur at high temperatures but does not exhibit the abrupt drop in intensity below the transition temperature as does pure sulfur.

### Introduction

Liquid sulfur undergoes a transition at 160 °C from a (low temperature) liquid consisting almost entirely of  $S_8$

rings to a (high temperature) mixture of high molecular weight polymer in equilibrium with  $S_8$ . At this temperature dramatic variations occur in the heat capacity, the viscosity, the fraction of polymerized material, the density, and the concentration of unpaired electrons (as measured by electron spin resonance (ESR)).

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