

Low-Energy Electron-Impact Study of the First, Second, and Third Triplet States of Benzene*

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The six lowest excited states of benzene have been investigated in the gas-phase free molecule at low pressure by electron-impact spectroscopy. Incident electron energies of 13.6 and 20.0 eV and scattering angles from 9° to 80° were used. Three singlet-singlet transitions at 5.0, 6.2, and 6.9 eV were identified. These transitions agree with the results of optical absorption and higher-energy electron-impact experiments. In addition, three triplet states were observed at 3.9, 4.7, and 5.6 eV. The positions of the first two triplet states agreed with optical data on solid benzene and threshold electron-impact experiments. The third triplet state at 5.6 eV was assigned on the basis of the relative intensity of the transition at various scattering angles. The ratio of the intensity of this transition to the allowed singlet-singlet transition at 6.9 eV was in a constant proportion to the corresponding ratio for the first triplet state (3.9 eV) at all scattering angles. The spacings of the first and second and second and third triplet states in benzene were determined to be 0.80 and 0.85 eV. The difference in the spacing is not significant with respect to experimental error.

INTRODUCTION

The excited electronic states of benzene have been the subject of many previous theoretical and experimental investigations. Work prior to 1965 has been well summarized by Herzberg.¹ The energies of the [0, 0] bands of the transitions to the first three singlet excited states are known to be 4.74, 6.02, and 6.85 eV. The first and third singlet states are of type $^1B_{2u}$ and $^1E_{1u}$, respectively. The assignment of the second singlet state is still in doubt and may be either $^1B_{1u}$ or $^1E_{2g}$. The first triplet excited state is generally considered to be either $^3B_{1u}$ or $^3B_{2u}$. More recently, the first and second triplet states of benzene have been investigated in the oxygen-perturbed absorption spectrum of low-temperature solid benzene by Colson and Bernstein.² These investigators measured the energy of the second triplet state as 4.56 eV above the ground state. This state is believed to be of type $^3E_{1u}$. Optical observation of the triplet states is extremely difficult since the absorptions are weak and low temperatures are necessary since there is a great deal of interference from the hot bands of nearby singlet-singlet transitions.

Theoretical work on the triplet states of benzene has been reviewed by Kearns.³ In addition to the two triplet states which have been observed optically, a third state is predicted in the 5–6-eV region. Platt⁴ has calculated the spacing of the triplet states of benzene as 0.49–1.3 eV. Obviously there is a need for experimental evidence on the location of this third triplet state.

In contrast to optical-absorption methods, the first triplet state of benzene can be observed with comparative ease in the electron-impact spectrum using the target molecule in the gas phase at a few mtorr pressure. We have previously observed this state using impact energies less than 20 eV and a scattering angle of 90°. The first triplet state has also been reported by Wei and Kuppermann⁶ who used a low-energy retarding-type electron spectrometer and has been observed by Compton *et al.*⁷ in a novel threshold experiment. The latter investigators also found a shoulder at 4.7 eV on the side of the first singlet-singlet transition which was assigned to the second triplet state in agreement with the optical work of Colson and Bernstein.² A weak feature at 5.4 eV was assigned to the third triplet state. It is apparently necessary to use a very low impact energy and large scattering angle since the failure of Lassette *et al.*⁸ to detect these singlet-triplet transitions in the 40–50-eV benzene energy-loss spectrum shows that they are quite weak with respect to the singlet-singlet transitions at higher energies.

In the course of further very low impact energy experiments with the fixed-angle, low-resolution electron spectrometer previously described,⁵ we noticed a persistent small peak in the energy-loss spectrum at 5.6 eV. When a new, variable-angle, high-resolution electron spectrometer was recently placed in operation, it was possible to conduct a detailed investigation of this and other transitions in the energy-loss spectrum at various primary energies and scattering angles. The results of the investigation are presented in this paper.

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¹ G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (D. Van Nostrand Co., Princeton, N.J., 1966), p. 555.

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³ D. R. Kearns, *J. Chem. Phys.* **36**, 1608 (1962).

⁴ J. R. Platt, *J. Mol. Spectry.* **9**, 288 (1962).

⁵ J. P. Doering and A. J. Williams III, *J. Chem. Phys.* **47**, 4180 (1967).

⁶ P. S. Wei, thesis, California Institute of Technology, 1968 (unpublished).

⁷ R. N. Compton, R. H. Huebner, P. W. Reinhardt, and L. G. Christophorou, *J. Chem. Phys.* **48**, 901 (1968).

⁸ E. N. Lassette, A. Skerbele, M. A. Dillon, and K. J. Ross, *J. Chem. Phys.* **48**, 5066 (1968).

EXPERIMENTAL

The electron spectrometer has been described elsewhere.⁹ The only alteration made for the present experiments was the installation of a larger second aperture in the analyzer collimator for some of the experiments reported here. This modification increased the scattered current by about one order of magnitude, but restricted the resolution to 100 meV. Because of the weak intensity of the scattering from the multiplicity and symmetry-forbidden transitions observed in these experiments, as well as some instability of the apparatus apparently caused by the benzene, 100-meV resolution was about as good as could be obtained in any case.

Reagent-grade benzene was used without further purification except for repeated outgassing in vacuum.

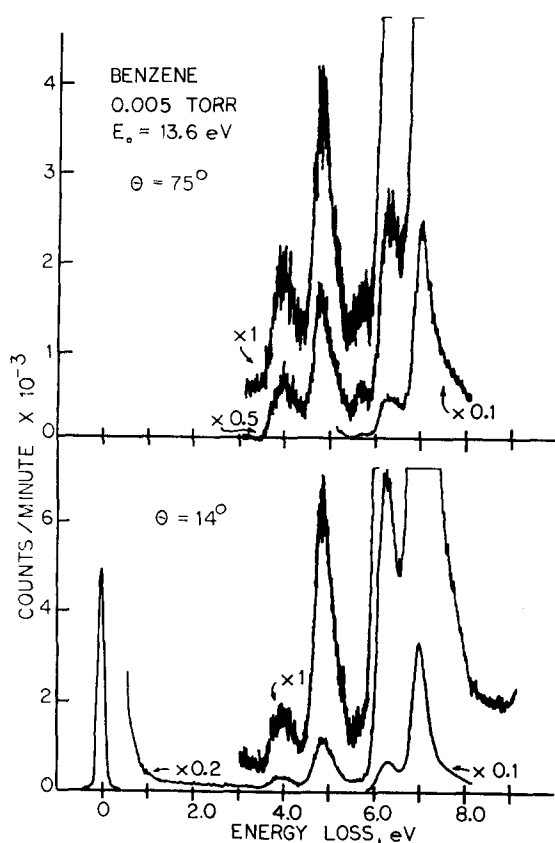


FIG. 1. Electron-impact spectra of benzene at 13.6-eV incident energy and scattering angles of 14° and 75°. The benzene pressure in the collision chamber was 0.005 torr. These spectra were taken using a count ratemeter (note scale changes). The elastic peak shown in the lower scan was attenuated by an unknown amount by lowering the electron-multiplier voltage so that only a small percentage of the multiplier output pulses were above the discriminator threshold. This peak is included to illustrate the energy resolution which was deliberately reduced to 180 meV for these scans.

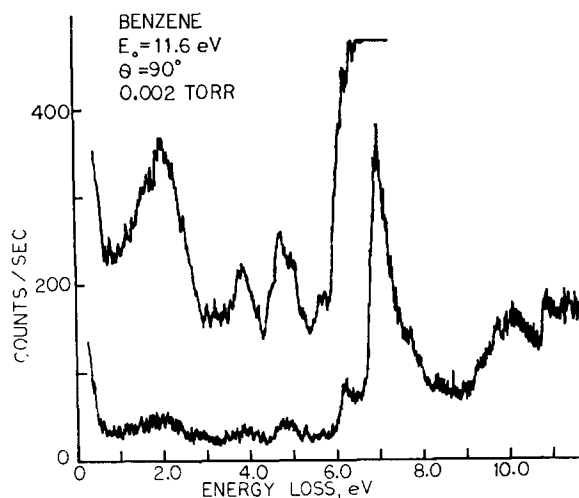


FIG. 2. Electron impact spectrum of benzene at 11.6-eV primary energy and 90° scattering angle taken with the low-resolution, fixed-angle instrument described in Ref. 5. The benzene pressure in the collision chamber was 0.002 torr. Note negative ion peak at 1.8 eV (Ref. 7).

Since the weakest singlet-triplet transition observed in these experiments was only a factor of 10^2 weaker than the adjacent singlet-singlet transitions, the extreme impurity problems which arise in optical-absorption experiments are not important in electron impact work.

RESULTS AND DISCUSSION

Preliminary experiments with the high-resolution, variable-angle electron spectrometer showed that the scattering from all states below 6 eV was quite weak at impact energies less than 20 eV and that spectra could be obtained at 100-meV resolution only by the use of long data-accumulation times. The resolution of the electron spectrometer was therefore reduced to 180 meV by retuning the analyzers in order to obtain spectra at various angles and primary energies in a reasonable amount of time. Since the electron-impact spectrum of benzene consists of a number of peaks composed of unresolved vibrational bands, the signal-to-noise ratio increases very rapidly with decreasing resolution. Figure 1 shows spectra of benzene taken under the reduced resolution conditions at 13.6-eV impact energy and 180-meV bandpass. There are five peaks in the spectrum at 75° including a small peak at 5.6 eV. Figure 2 shows a benzene spectrum at 90° scattering angle and an incident energy of 11.6 eV taken with the fixed-angle, low-resolution instrument described previously.⁵ The small inelastic process at 5.6 eV was always present in spectra at this energy from the older instrument, but the signal-to-noise ratio was not good enough to allow further studies. The observation of this peak in spectra from two quite different electron-scattering instruments is convincing evidence that the feature is not an experimental artifact.

⁹ A. J. Williams III and J. P. Doering (preceding paper).

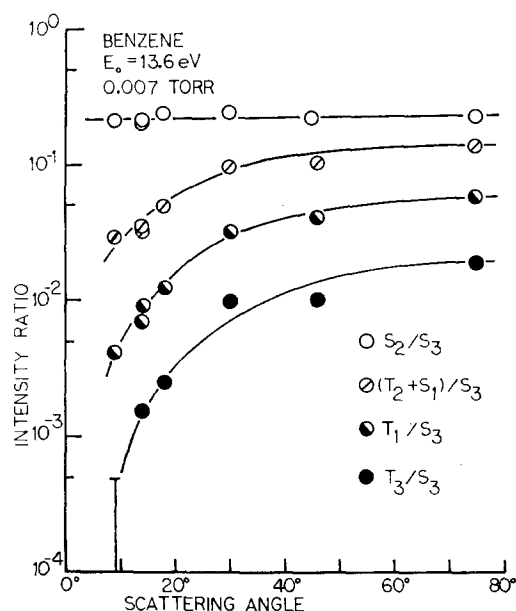


FIG. 3. Intensity ratios of various transitions in the benzene electron-impact spectrum vs scattering angle taken from a number of spectra similar to those in Fig. 1. The bar for the ratio T_3/S_3 represents the upper limit which could be placed on the intensity of this transition from the 9° scattering spectrum. The incident energy used was 13.6 eV. The singlet- and triplet-state symbols are defined in the text.

The five peaks in the 75° spectrum of Fig. 1 are at 3.9, 4.8, 5.6, 6.2, and 6.9 eV. The 3.9-eV peak is the first triplet state which we have previously reported.⁵ The 4.8-eV peak is a combination of the second triplet state at 4.7 eV and the first singlet state whose vibrational bands (resolved by Lassette *et al.*⁸) extend from 4.7–5.2 eV. Under the low-resolution conditions of the spectrum in Fig. 1, it was not expected that we could resolve the two transitions. The relative intensities of the singlet and triplet states at this energy will be discussed below. The 5.6-eV peak can be tentatively assigned to the third triplet state from the spectra of Fig. 1 since it obviously becomes weak compared to the singlet-singlet transitions at small scattering angle. The 6.2- and 6.9-eV peaks are the second and third singlet states, respectively.

Since the symmetries of certain of the benzene states are not known at the present time and the electron-impact experiments reported in this paper do not give any information which would allow the symmetries to be assigned with greater certainty, it seems preferable to refer to the states by their multiplicities and relative energies to avoid the possibility of perpetuating incorrect assignments.¹⁰ For the purposes of this paper, the three lowest singlet states are designated S_1 , S_2 , and

S_3 in order of increasing energy above the ground state. Similarly, the first three triplet states are designated T_1 , T_2 , and T_3 .

Data on the relative intensities of the various peaks in the energy-loss spectrum obtained from spectra similar to the ones in Fig. 1 are shown in Figs. 3 and 4. In Fig. 3, the ratios of the intensities of the first three triplet and first two singlet states with respect to the intensity of the allowed transition to the third singlet state are plotted as a function of scattering angle. The data in this figure were all taken at an impact energy of 13.6 eV. Similar data taken at 20-eV impact energy are presented in Fig. 4. The data are quite similar at the two impact energies, but the ratios T_1/S_3 and T_3/S_3 are somewhat larger at the lower impact energy as would be expected. The most dramatic difference in the behavior of the various transitions is in the ratio of the two singlet-singlet transitions S_2/S_3 contrasted to the triplet-singlet ratio T_1/S_3 . The two singlet-singlet transitions remain in constant proportion over a range of scattering angles from less than 10° to 80° . The singlet-triplet to singlet-singlet ratio, however, increases by an order of magnitude over the same angular range.

Since there is little doubt that the 3.9-eV state T_1 is actually a triplet state and that the 6.96-eV state S_3 is a singlet, the behavior of the ratio T_1/S_3 can be used as a standard to which the behavior of the other states can be compared. The ratio T_3/S_3 is proportional to the ratio T_1/S_3 within experimental error over the entire range of scattering angles studied at both primary

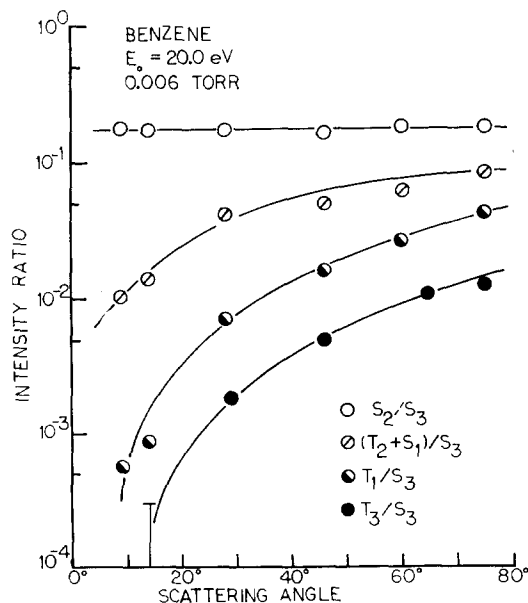


FIG. 4. Intensity ratios of various transitions in the benzene electron impact spectrum vs scattering angle for 20-eV incident energy. The bar at 14° for the ratio T_3/S_3 indicates the upper limit for the intensity of this transition at 14° .

¹⁰ The author is indebted to Professor R. Hochstrasser for a discussion of this point.

energies. This fact gives strong support to the assignment of the 5.6-eV peak as a singlet-triplet transition. The ratio of the 4.9-eV peak, which consists of the unresolved combination of the second triplet and first singlet ($T_2 + S_1$), to the third singlet does not vary as much with increasing scattering angle as the ratios for the two triplet states discussed above. The first singlet-triplet transition in benzene is symmetry forbidden and occurs by vibrational distortion of the benzene ring.¹ We might, therefore, expect an intermediate scattering behavior from this transition. The ratio for the 4.9-eV peak to the third singlet in Fig. 3 at 20-eV incident

energy extrapolates at zero angle to a value of approximately 2×10^{-3} . The data presented by Lassettre *et al.*⁸ show a 40-eV, 0° spectrum of benzene in which the ratio of the first singlet state to the third singlet state is approximately 5×10^{-3} . If it is assumed that the ratio does not change significantly between 20- and 40-eV impact energy, there is order-of-magnitude agreement of the former result with what would be expected if the 4.9-eV peak were mainly due to the singlet-singlet transition at small angles as in the spectrum of Lassettre *et al.*⁸ At larger angles, it is expected that the singlet-triplet transition will become increasingly important. The data are therefore consistent with what would be expected for the behavior of these states as seen in a low resolution spectrum.

Further information on the relative intensities of the two states in the 4.9-eV region is given by the higher resolution spectra shown in Fig. 5. To obtain these spectra, the size of the second collimator aperture in the analyzer was increased as previously described. The resolution of approximately 100 meV used for these experiments was not sufficient to resolve any vibrational structure; but the vibrational bands may be complicated by the overlapping singlet and triplet states which appear under these conditions. The vertical bars and symbols represent the positions of the states assigned from the data given above. At 9° scattering angle, the unresolved 4.9-eV peak of Fig. 1 appears at 5.0 eV. This result is in agreement with the 40-eV resolved spectrum of the first singlet-singlet transition given by Lassettre *et al.*⁸ since the strongest vibrational component in their spectrum is at 5.017 eV. Because of the small scattering angle and decreased angular resolution, there is a great deal of background in the 9° spectrum of Fig. 5. The 23° spectrum is similar to the 9° spectrum except that the background is lower at the larger scattering angle. However, at 54° , the peak at 5.0 eV has disappeared and a second peak at 4.75 eV has appeared. This observation is consistent with the earlier conclusion that the singlet-singlet transition was dominant at small angle and that most of the intensity in the lower resolution spectra at large angles was due to the singlet-triplet transition. These higher resolution data also make possible a more accurate determination of the energies of the states than was possible with the lower resolution spectra. The best values for the Frank-Condon maxima of the three triplet states are 3.95, 4.75, and 5.60 eV with an uncertainty of ± 0.050 eV in each case.

The dramatic increase in the relative intensity of the transition to the third triplet state is well illustrated by the spectra in Fig. 5. In the small-angle spectrum, there is enough intensity in the higher vibrational bands of the first singlet-singlet transition extending above 5.5 eV to make observation of the third triplet state impossible. At the small angles, even the relatively intense transition to the first triplet state, T_1 , is not

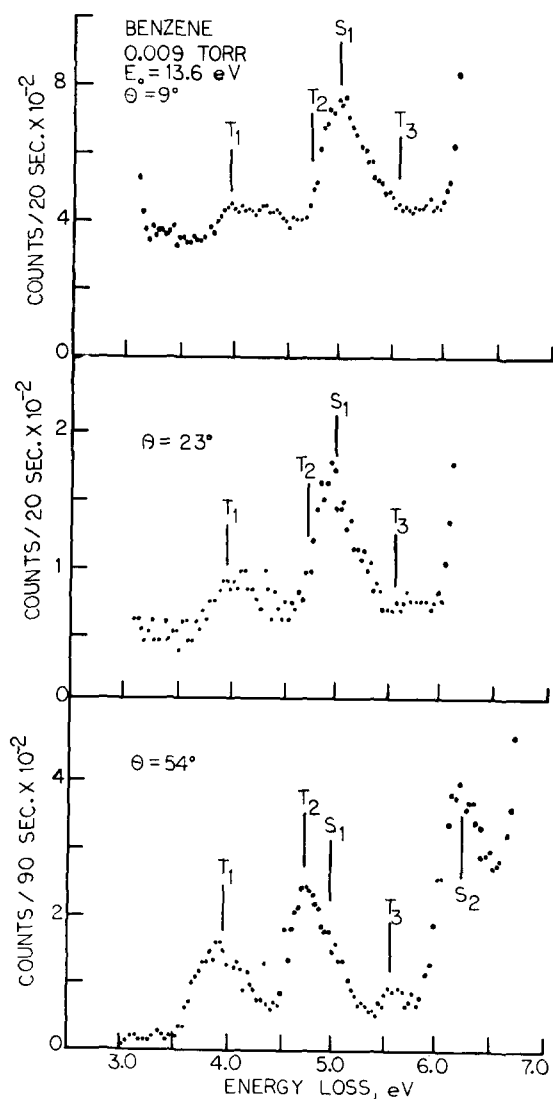


Fig. 5. Electron-impact spectra of benzene at 13.6-eV incident energy and scattering angles of 9° , 23° , and 54° . The singlet- and triplet-state symbols are defined in the text. Note shift of position of peak at 4.7–5.0 eV with increasing scattering angle. These spectra were taken using multiple scans of the 128 channel analyzer. An accumulation time of 10 sec/channel was used for each scan.

very clear. These results demonstrate the necessity for very low incident energies and large scattering angles in the search for weak singlet-triplet transitions of this type since hot bands and other vibrational structure from adjacent intense singlet-singlet transitions cause so much background at small scattering angles and higher energies that the singlet-triplet transitions cannot be observed.

CONCLUSIONS

The experiments reported in this paper locate the three lowest triplet excited states of benzene at 3.95, 4.75, and 5.60 eV with an uncertainty of ± 0.05 eV in all cases. These energies refer, of course, to the Frank-Condon maxima of the transitions which should not be confused with the positions of the $[0, 0]$ bands. The $[0, 0]$ band positions cannot be accurately determined from the present experiment. In any case, it is difficult to characterize these transitions by a single energy for comparison with theoretical calculations since the peaks observed in the electron-impact spectra consist of unresolved vibrational structure which extends in many cases over 0.5 eV or more. Lassettre *et al.*⁸ have succeeded in resolving some vibrational structure of the first and second singlet-singlet transitions, but it is not clear how far the bands can be resolved since they may be inherently diffuse. In the present case, very high resolution will be required to resolve the transitions which appear at large scattering angles since there is undoubtedly a large amount of overlapping vibrational structure.

Lassettre *et al.*⁸ have also noted a change in relative intensities of the vibrational bands of the second

singlet-singlet transition at 6.2 eV with scattering angle for angles less than 8° and have concluded that two electronic states are involved in this region of the energy-loss spectrum. The present results show that the ratio of the unresolved 6.2-eV peak to the 6.95-eV third singlet-singlet transition is constant over a wide range of scattering angles greater than 9° . If two states are involved in this energy region, therefore, one must be important only at small scattering angles since the large-angle scattering behavior is what would be expected for a single state.

The triplet-state energies determined from the present experiment are in agreement with the optical work of Colson and Bernstein² and the threshold experiment of Compton *et al.*⁷ as to the positions of the first two triplet states. Compton *et al.*⁷ reported that the feature they identified as the third triplet state at 5.4 eV was not always present in their spectra, and since this was at best a weak feature, the agreement of the present experiment with their results can be regarded as satisfactory.

The spacing of the Frank-Condon maxima of the first two triplet states is 0.80 eV and that of the second and third states is 0.85 eV. The difference is not significant with respect to experimental error, so the present experiments show that the spacings are essentially identical to within at least 0.10 eV. The spacing falls well within the theoretical limits calculated by Platt.⁴ The 54° scattering spectrum in Fig. 5 gives a good idea of the relative intensities of the three singlet-triplet transitions. The strongest is the second, T_2 . The first, T_1 , is intermediate in intensity, and the third, T_3 , is the weakest.