

High resolution electron impact studies of electric dipole-forbidden states of benzene

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Abstract. Electron energy-loss spectra have been obtained, with a resolution of 0.030 eV for the electronic states of benzene below 11.5 eV. Spectra were accumulated using both high (100 eV) and low (10 eV) scattered-electron energies and a range of scattering angle between 0.5 and 60 degrees. At high scattering angles prominent vibrational structure has been observed in the first three triplet bands ($^3B_{1u}$, $^3E_{1u}$, and $^3B_{2u}$). A progression of three levels starting at 6.10 eV has been observed for the first time, and assigned to the $^3E_{2g}$ valence state. The intensity of the energy loss peak at 6.32 eV has been measured over a range of scattering angles and the angular distribution found to be consistent with its previous assignment as an electric quadrupole transition. Rydberg states converging to the first and second ionisation potentials have been studied and in both cases quadrupole transitions have been detected for the first time. A series of four such levels converge to the first ionisation potential with a quantum defect of 0.266, and the Rydberg orbital is identified as $nd(a_{1g})$. Two quadrupole transitions converging to the second ionisation limit have a similar quantum defect of 0.226 and are believed to involve transitions from the $3e_{2g}$ orbital to the same Rydberg orbital.

1. Introduction

In many ways the benzene molecule is a corner-stone in the study of quantum chemistry, molecular spectroscopy, and photochemistry, and its electronic structure has long been the subject of intense theoretical and experimental interest. Work prior to 1975 has been well reviewed by Robin (1975). Despite the great wealth of experimental work using optical spectroscopic techniques, only six valence states of benzene have been convincingly identified. These states comprise the singlet and triplet $\pi \rightarrow \pi^*$ states of symmetries B_{1u} , B_{2u} , and E_{1u} , formed by promoting an electron from the highest filled orbital ($1e_{1g}$) to the lowest unfilled orbital ($1e_{2u}$).

Of these six states, only the $^1E_{1u}$ state is fully allowed by dipole-selection rules, the symmetry-forbidden $^1B_{1u}$ and $^1B_{2u}$ states being weakly allowed due to vibronic coupling with the $^1E_{1u}$ state via an e_{2g} vibrational mode. The remaining electronic states, both singlet and triplet, have been the subject of investigations using a variety of techniques including phosphorescence studies (e.g. Ivanova and Sveshnikov 1961), multiphoton ionisation spectroscopy (Vaida *et al* 1978), photoabsorption spectroscopy using high pressure oxygen perturbation (e.g. Evans 1957, King and Pinnington 1965), Raman spectroscopy (Ito *et al* 1978), electron energy-loss spectroscopy (Lassette *et al* 1968, Doering 1969, 1977), and threshold electron spectroscopy (Brongersma *et al* 1969, Compton *et al* 1968).

In this paper we present the most complete electron impact study of the benzene molecule to date. Previous studies using the technique of energy-loss spectroscopy at low impact energies and high scattering angles (e.g. Trajmar *et al* 1970, Wilden *et al* 1977, 1979, Wilden and Comer 1979) have shown that the technique can be used to detect spin or symmetry-forbidden transitions with high sensitivity. With the exception of a recent study by Doering (1977) the resolution obtained in previous low energy, high angle energy-loss studies has been limited to about 0.12–0.18 eV (FWHM), and consequently no vibrational structure was resolved. The threshold spectrum of benzene has also been studied with similar resolution, using the retarding field technique (Brongersma *et al* 1969) and the SF_6^- scavenging technique (Compton *et al* 1968). Despite the relatively low resolution, compared with optical techniques, the early electron impact investigations detected many forbidden transitions: of particular importance are the angular distributions measured by Doering (1969) which confirmed the spin multiplicities of several states of benzene.

In the recent study by Doering (1977), energy-loss spectra of the triplet and singlet states were presented with a significantly better instrumental resolution (0.075 eV FWHM) allowing some vibrational structure to be resolved. In the present paper a resolution of 0.030 eV has been employed, representing considerable further improvement. In addition, the signal-to-noise ratio is much improved compared with previous studies. For these reasons additional vibrational levels have been detected and their excitation energies accurately determined. In the present work we have also investigated two regions of the energy-loss spectrum using the low energy, high angle technique for the first time. These regions are from 6.0 to 6.5 eV which was previously studied by Lassetre *et al* (1968) using higher energy excitation and the Rydberg region (7.0–12.0 eV) which has not been systematically studied using electron impact.

2. Experimental

The electron spectrometer used for the present measurements has been fully described elsewhere (Wilden *et al* 1976). Briefly, a crossed beam scattering geometry was employed, with a single capillary forming the molecular beam, and an electron analyser and monochromator defining the energies of the scattered and incident electrons. A coplanar scattering geometry was used, and the scattering angle could be varied between about 0.5 and 60 degrees.

The benzene used had a purity of 99.9% and was used following freeze/pump/thaw cycles to remove dissolved gases. The electron monochromator and analyser were not differentially pumped and operated satisfactorily with the typical background pressure of 5×10^{-6} Torr of benzene vapour (uncorrected ion gauge reading) used in the present measurements. The gas pressure at the scattering region, near the tip of the capillary is difficult to estimate because of the unknown but significant pumping action of a liquid nitrogen-cooled vapour trap between the vacuum chamber and the diffusion pump.

3. Results

Energy-loss spectra of benzene were accumulated in the constant residual energy mode, in which the residual energy of the scattered electrons detected was held constant and the incident electron energy was scanned. This method has several advantages when studying energy-loss spectra at low incident energies (Wilden *et al* 1979).

The spectra were measured using residual energies in the range 5 to 100 eV, and at a number of scattering angles up to 60 degrees. The instrumental resolution, which contains contributions from both hemispherical deflectors was typically 0.030 eV (FWHM) for the spectra discussed in this work. Accumulation times varied from 30 minutes to several hours depending in the scattering angle.

In figure 1, the energy-loss spectra covering the region 3.0 to 7.5 eV are shown for three types of excitation conditions, namely high residual energy and low scattering angle (figure 1(a)), low energy and low angle (figure 1(b)), and low energy and high angle (figure 1(c)). The excitation energies of features observed in these spectra are summarised in table 1. In figure 2, spectra are presented which show systematic changes in features in the 5.5 to 6.5 eV energy-loss region as the scattering angle is varied in the range 0.5 to 60 degrees. The angular dependence of two features visible in these spectra are shown in graphical form in figure 3.

Energy-loss spectra of the Rydberg state region up to the first ionisation potential are shown in figure 4 for a range of excitation conditions. Similar measurements for Rydberg series converging to the second ionisation potential are shown in figure 5.

4. Discussion

4.1. Instrumental resolution

The problem of establishing the instrumental resolution for spectra of a large polyatomic molecule is by no means trivial, because the complicated vibrational band structure which accompanies most electronic transitions often broadens apparently single peaks.

In the present study, the spectrometer was tuned to give a consistent resolution of 0.025 to 0.030 eV (FWHM) on the relatively sharp energy loss bands of N₂, but we consider it necessary to present the following evidence that comparable resolution was achieved for benzene.

(i) A clear demonstration of the resolution is claimed only for spectrum (a) of figure 1. In high resolution photoabsorption spectra (e.g. Pantos *et al* 1978) each ¹B_{2u} level resolved in the present work is split into an intense level with weaker, closely-spaced peaks at lower energy. In our spectrum, these unresolved levels cause a distinct asymmetry in the observed peaks, and lead to a relatively high full width at half maximum (~0.05 eV). However the half width at half maximum, measured on the sharp, high energy side of the peak is only 0.015 eV, consistent with the claimed instrumental resolution of 0.030 eV (FWHM).

(ii) For the remaining benzene spectra, no sufficiently isolated peak could be found on which to measure the resolution. The spectrometer was tuned in the same way as above, but the possibility of the broadening effect of any drift in the energy loss with time must still be considered. To check this possibility, we have recorded energy-loss spectra of a benzene/N₂ mixture over a long collection time (20 hours). The instrumental resolution, measured on the LBH bands of N₂ was found to be 0.033 eV (FWHM).

4.2. Low-lying $\pi \rightarrow \pi^*$ states

The lowest $\pi \rightarrow \pi^*$ transition in benzene gives rise to six electronic states, comprising the singlet and triplet states of symmetry B_{1u}, B_{2u}, and E_{1u}. The three singlet states have

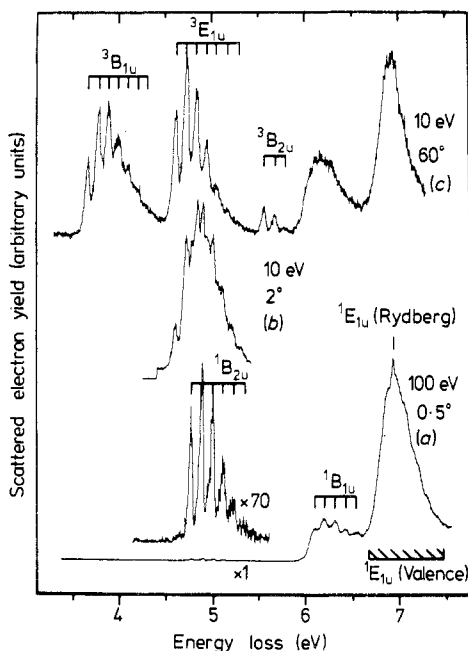


Figure 1. Energy loss spectra of benzene in the energy loss range 3.5 to 7.5 eV. The scattering angle and the residual energy of the scattered electrons detected are shown beside each spectrum.

been well studied using optical techniques (see the reviews by Herzberg 1966, and Robin 1975). The singlet states are clearly shown on figure 1(a) which was obtained using a high residual energy (100 eV) and near forward scattering angle, under which conditions the Born approximation is approximately valid, and optical selection rules apply. The spectrum is primarily presented for comparison with the spectra obtained with lower residual energies (figures 1(b), (c)). The weakness of the symmetry-forbidden transition to the ${}^1B_{2u}$ state should be particularly noted. In agreement with the spectra of Lassette *et al* (1968), no evidence for singlet-triplet transitions was found on the spectrum.

In contrast, when the low energy, high scattering angle conditions were used (figure 1(c)), all three singlet-triplet transitions were prominently observed, as well as the singlet-singlet transitions. This result is consistent with the angular distributions of Doering (1969). In previous studies of the energy-loss spectrum of benzene at high scattering angles, the energy resolution and sensitivity have been relatively poor, and little or no vibrational structure was revealed. The present resolution (0.030 eV FWHM) represents more than a factor of two improvement. The excitation energies of the features observed in figure 1(c) are summarised in table 1, and discussed below.

The first triplet state, ${}^3B_{1u}$, has been studied using the optical O_2 perturbation technique, in which UV absorption to triplet states is enhanced by the presence of high pressures (typically 100 atm) of O_2 in the absorption cell. The excitation energies obtained by Evans (1957), Colson and Bernstein (1965), King and Pinnington (1965), and Metcalfe *et al* (1974) are listed in table 1. With the exception of the work by King and Pinnington, the resolution obtained by this technique is inferior to the present

Table 1. Comparison of the excitation energies for levels of the first three triplet states of benzene, as measured in electron impact studies (columns 2 and 3) and in optical studies using the O₂ perturbation technique.

State	Excitation energies (eV)					
	Electron impact		Optical studies			
	Present work	a	b	c	d	e
³ B _{1u}	3.528					
	3.571					
	3.665	3.67	3.659	3.659	3.679	3.658
				3.689		
	3.780	3.79	3.771	3.771	3.792	3.782
				3.801		
	3.880	3.89	3.881	3.878	3.899	3.881
				3.910		
	3.990	3.98	3.981	3.978	3.999	3.992
	4.100		4.089	4.091		4.092
³ E _{1u}	4.210			4.212		
	4.321			4.339		
					4.533	
	4.610	4.63			4.608	
	4.715	4.73				
	4.830	4.85				
	4.940	4.95				
	5.050					
	5.170					
³ B _{2u}	5.560	5.58				
	5.680	5.69				
	5.790	5.81				

a, Doering (1977); b, Evans (1957); c, Colson and Bernstein (1965); d, King and Pinnington (1965); e, Metcalf *et al* (1974).

electron-impact study. In the former work, the first three levels were resolved into closely spaced doublets, which were not observed in the present spectra.

The energy of the electronic origin of the ³B_{1u} state is known to be 3.659 eV, from the phosphorescence measurements (Ivanova and Sveshnikov 1961). This level would not be expected to appear in our spectra or the O₂ perturbation spectra because the transition A_{1g} → B_{1u} is symmetry-forbidden in the normal benzene point group of D_{6h}. In fact this level is strongly observed in both techniques. King and Pinnington discussed the possibility that the level appears on their spectra as a result of a lowering of symmetry to D_{2h} due to the perturbing O₂ molecules. This explanation is not valid for the present results, and it is more likely that the triplet geometry is intrinsically distorted, as indicated by ESR measurements (de Groot and van der Waals 1963).

The two very weak peaks at 3.53 and 3.57 eV have not been noted previously, but appear on all our spectra taken with similar scattering conditions. Their position and weakness indicate that they may be hot bands, associated with transitions from excited vibrational levels of the ground state.

Figure 1(a) clearly shows that the intensity of the $^1B_{2u}$ state is very low compared with the $^1E_{1u}$ band. Consequently in figure 1(c) the relatively intense band between 4.6 and 5.17 eV must be assigned to a second spin-forbidden transition, in agreement with the angular distributions measured by Doering (1969). This second triplet band $^3E_{1u}$ has not been investigated as thoroughly as the first triplet state by optical techniques, since it is strongly overlapped by the relatively intense $^1B_{2u}$ band with its associated hot bands. In the energy-loss spectra of Doering (1977) four vibrational levels of the second triplet state were resolved, whereas in previous energy-loss spectra (Doering 1969, Frueholz *et al* 1977) and in threshold spectra (Compton *et al* 1968) the triplet state was observed only as an unresolved shoulder. In the present spectra seven levels of the second triplet state are observed, and their measured energies are listed in table 1 together with the measurements of Doering (1977). Also shown are the excitation energies of two levels detected in the only O_2 perturbation photoabsorption study of this region (Colson and Bernstein 1965). No evidence for the first level seen in the latter work could be observed on our spectra, and the possibility must be considered that this level arose from an impurity.

The existence of two separate electronic states in this region of the spectrum is clearly demonstrated in figure 1(b). Here the intensity of the triplet state has been reduced to a similar level as the $^1B_{2u}$ state, by reducing the scattering angle to near 0° . In the resulting spectrum, vibrational series of both states can be distinguished.

The third triplet state, $^3B_{2u}$, has been observed only in electron impact spectroscopy (Compton *et al* 1968, Doering 1969, 1977). The energies of the three vibrational levels observed in the present spectra are compared, in table 1, with the measurements of Doering (1977). The angular behaviour of this triplet state is consistent with the published angular data of Doering (1969). The intensity distribution across the three levels is quite different from that of the other $\pi \rightarrow \pi^*$ bands and probably indicates that the equilibrium geometry is different.

4.3. 6 eV to 6.5 eV region

A fourth low-lying $\pi \rightarrow \pi^*$ state, $^1E_{2g}$ together with its triplet counterpart is predicted to arise from excitation of an electron from the π -bonding $1a_{2u}$ orbital to the lowest unfilled orbital ($1e_{2u}$). Transitions to this state are forbidden by electric dipole radiation, but allowed by electric quadrupole radiation selection rules.

Lassette *et al* (1968) presented evidence from electron impact spectroscopy that such a quadrupole-allowed transition may exist at an energy of 6.2 eV, superimposed on the diffuse levels of the $^1B_{1u}$ state. This conclusion is based on the observation that the level at 6.20 eV increased in intensity relative to the levels either side of it, as the scattering angle was increased. These measurements were made with high impact energies (50 and 90 eV), low scattering angles (0–8 degrees) and relatively good resolution (0.04 eV). Recently Doering (1977) has studied this region with lower impact energies (12 and 40 eV) and higher angles (20, 30 and 70 degrees) and concluded that the angular and energy behaviour of the peak was complicated, although with the available resolution (0.075 eV) and poor statistics, the structure was not well resolved.

The present spectra, shown in figure 2 represent the first systematic study of the angular dependence of states in this region at low impact energies. The spectra presented cover the range 2–60° in scattering angle at a scattered electron energy of 10 eV and a constant resolution of 0.040 eV (FWHM). The 100 eV, 0.5° spectrum

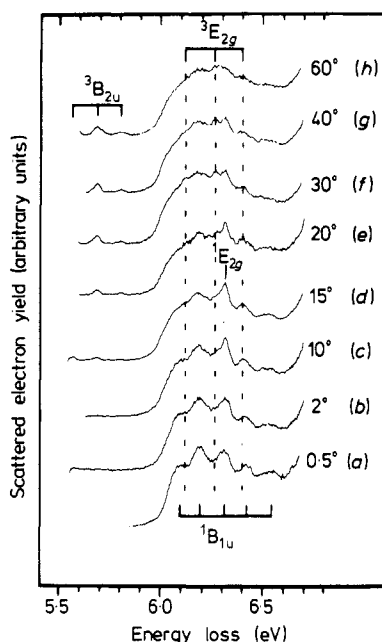


Figure 2. Energy loss spectra of the 5.6–6.6 eV region. The scattering angle is shown beside each spectrum. The residual energy of the scattered electrons was fixed at 100 eV for spectrum a and 10 eV for the other spectra. The spectra have been plotted so that their vertical heights are approximately constant for convenience. The average count rates varied between 5000 counts/s (spectrum (a)) and 100 counts/s (spectrum (h)).

(figure 2(a)) is shown for comparison, and is in good agreement with the UV photoabsorption spectrum of Pantos *et al* (1977). Our measurements of the energies of features in this region are summarised in table 2, and our assignments are discussed below.

In the two spectra collected with the smallest scattering angle (figures 2(a), (b)), a simple progression of five broad peaks is observed. The assignment of this band to the $^1B_{1u}$ state is discussed by Robin (1975). Between 10° and 20° (figures 2(c)–2(e)), one energy-loss peak at 6.32 eV becomes enhanced, in agreement with the high energy electron energy-loss spectra of Lassettre *et al* (1968). This peak is relatively sharp compared with the underlying $^1B_{1u}$ level, and the wings of the latter state can be seen to low energy of the sharp peak. As the scattering angle is further increased between 30° and 60° (figures 2(f)–2(h)) the intensity of the sharp feature becomes weaker.

For each of the spectra shown in figure 2 we have estimated the height of the peak of the 6.32 eV structure above the smooth continuum formed by the overlapping $^1B_{1u}$ levels, and divided this by the height of the $^1B_{1u}$ background at the same energy. The variation of this ratio with scattering angle is plotted in figure 3 and indicates how the intensity of the peak at 6.32 eV varies relative to a singlet–singlet transition. Trajmar *et al* (1970) presented evidence from many molecules that the intensity ratio for singlet–triplet transitions increases strongly, and monotonically as the scattering angle is increased up to 60°. This is borne out by the second curve in figure 3 which shows our measurements of the intensity of a level of the $^3B_{2u}$ state relative to the same $^1B_{1u}$ level. On this evidence the assignment of the 6.32 eV feature to a singlet–triplet transition can be ruled out. Furthermore the low intensity of the feature on the low angle spectra is

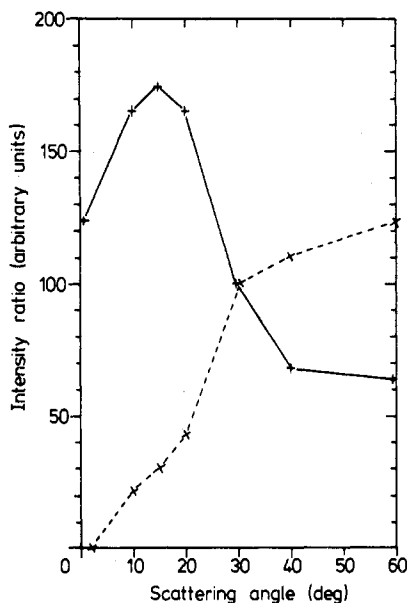


Figure 3. Measurements of the intensity of the 6.32 eV feature at a number of scattering angles. The full curve shows that ratio of the estimated intensity of the 6.32 eV peak to that of the underlying $^1B_{1u}$ background. The broken curve shows the same ratio for the triplet level at 5.68 eV for comparison.

not consistent with a dipole-allowed transition. In conclusion the assignment of the state to the quadrupole-allowed $^1E_{2g}$ state (Lassettre *et al* 1968) is consistent with the present angular measurements. A second possibility is that this feature could be assigned to a transition involving excitation of the outermost valence electron to the $3s(a_{1g})$ Rydberg orbital, which would also produce a quadrupole-allowed $^1E_{2g}$ state. This is supported by the fact that only a single vibrational level is observed, as is the case for the dipole-allowed $^1E_{1u}$ Rydberg state at 6.94 eV. With this assumption the measured quantum defect for the state would be 0.84, close to the value of 0.8 predicted for this Rydberg series by Jonsson and Lindholm (1969). However, our measurements in the energy-loss range 7.5 to 9.5 eV (§ 4.4) show no evidence for higher members of the series with this quantum defect.

As can be seen from table 2, the energy of 6.32 eV is very close to the excitation energy of 6.33 eV measured for a feature in the two-photon spectrum of Vaida *et al* (1978), but does not agree with the energies assigned to the $^1E_{2g}$ state in the study of benzene in krypton and xenon matrices (Taleb *et al* 1970, Morris and Angus 1973).

At higher scattering angles the present spectra (figures 2(f)–2(h)) show evidence for further singlet–triplet transitions in the 6 to 6.5 eV energy-loss region. The most prominent such feature, (at 6.27 eV) increases strongly in intensity between 20 and 60 degrees but has not been resolved in previous studies. A second level at 6.39 eV is resolved from the nearby $^1B_{1u}$ level on figure 2(e) and its presence on figures 2(g) and 2(h) can be inferred from the shift of the maximum of the structure away from the position of the $^1B_{1u}$ level (6.32 eV). There is also indirect evidence for a third level at about 6.13 eV on the high-angle spectra. On the spectra in figures 2(a) and 2(b) this energy corresponds to a distinct plateau between the $^1B_{1u}$ levels at 6.10 and 6.19 eV, but as the scattering angle is increased the plateau is progressively filled in.

Table 2. Measured energies of features in the 6.0 to 6.6 eV region. Also shown are the excitation energies derived in previous electron impact and optical studies.

State	Present	Excitation Energy (eV)			
		a	b	c	d
$^1B_{1u}$	6.095				
	6.195				
	6.315				
	6.425				
	6.550				
$^1E_{2g}$	6.32	6.3		5.68 5.74	6.33
$^3E_{2g}$	6.110				
	6.270				
	6.395				
			6.55		

a, Lassettre *et al* (1968); b, Astier *et al* (1969); c, Taleb *et al* (1973); d, Vaida *et al* (1978).

The high-angle intensity variation of the three levels discussed above is strong evidence for their assignment to singlet-triplet transitions. The three triplet levels detected, at 6.13, 6.27, and 6.39 eV form a series with a mean spacing of 0.13 eV, which is close to the energy of the totally-symmetric breathing mode (ν_2) of benzene (Herzberg 1966). *Ab initio* (Hay and Shavitt 1974) and semi-empirical calculations (Pariser 1956, Visscher and Falicov 1970) predict that the fourth triplet state is the $^3E_{2g}$ valence state or the $^3E_{1u}$ Rydberg state, lying in the range 5.9 to 7.3 eV. The $^1E_{1u}$ Rydberg state is recognised (Robin 1975) as a sharp peak at 6.93 eV, superimposed on the broad $^1E_{1u}$ valence state. The assignment of the triplet band to the triplet counterpart of this state would imply a singlet-triplet splitting of 0.8 eV which is unlikely for a Rydberg state. Consequently the alternative assignment, to the $^3E_{2g}$ valence state is suggested. Astier and Meyer (1969) reported a triplet-triplet absorption in liquid benzene to a state at 6.55 eV which has also been assigned to the $^3E_{2g}$ state. No evidence for the existence of this state is provided by the present spectra, although we estimate that the fourth member of the progression we observe would lie at a similar energy (6.52 eV).

4.4. Rydberg states converging to the first ionisation potential

In optical absorption studies, four Rydberg series are known to converge to the first IP (9.248 eV). Two of the series, designated R and R' (Price and Wood 1935) are intense, have quantum defects of 0.46 and 0.16, and have been assigned (Betts and McKoy 1971, Jonsson and Lindholm 1969) to the allowed transitions $1e_{1g} \rightarrow np(a_{2u})$ and $1e_{1g} \rightarrow np(e_{1u})$. Members of two additional series, R'' and R''', lie close to members of the R' series with quantum defects of 0.11 and 0.05 respectively. The weakness of these levels led to their assignment to the optically-forbidden transitions $1e_{1g} \rightarrow nd(e_{1g})$ and $1e_{1g} \rightarrow nd(e_{2g})$ (Betts and McKoy 1971) which gain intensity via vibronic coupling to allowed transitions. Recent measurements by Okenga *et al* (1979b) have led to a revision of the quantum defects of the three series R' to R''' to the values 0.08, 0.055,

and 0.01 respectively and alternative assignments involving $nf(a_{2u}, e_{1u} \text{ and } e_{2u})$ orbitals were presented. Transitions to two final series, involving $ns(a_{1g})$ and $nd(a_{1g})$ Rydberg orbitals are also electric dipole forbidden and have not been experimentally observed. The purpose of the present investigation was to attempt to identify these latter transitions using the less rigorous electron impact selection rules.

In our spectra at high impact energy, figure 4(i), good agreement is noted with the UV absorption spectra (e.g. Price and Wood 1935, Koch and Otto 1972). The two main optically-allowed series are assigned on the diagram. As the scattering angle is increased in the range 0.5 to 10 degrees, systematic changes in the intensity of at least six levels, labelled a to f are noted when their intensities are compared with the R and R' series. The angular variation of the intensities of these peaks is similar to that of the peak at 6.32 eV discussed in § 4.3. These levels are therefore also assigned to singlet, quadrupole-allowed transitions.

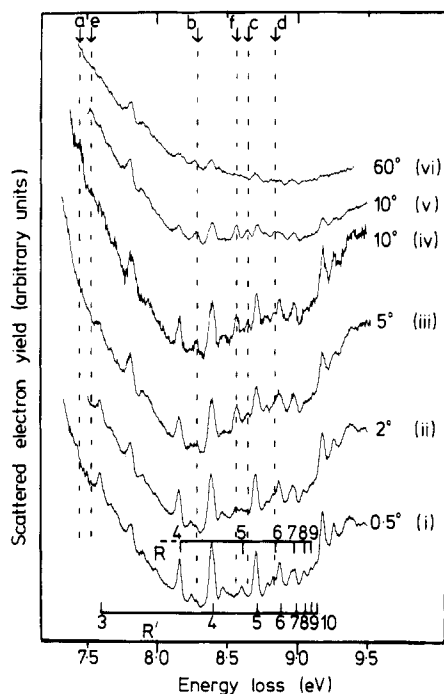


Figure 4. Energy loss spectra showing Rydberg series converging to the first ionisation potential. The optically-allowed series R and R' are indicated: a further two optically observed series are discussed in the text but were not resolved in the present work. The scattering angle used is indicated beside each spectrum. The residual energy of the scattered electrons was fixed at 100 eV for spectra (i)–(iv) and 10 eV for spectra (v)–(vi). The six levels marked with arrows have been assigned to quadrupole-allowed transitions in the present work.

The excitation energies of the four peaks a–d are in excellent agreement with the energies calculated using the Rydberg formula, with a quantum defect of 0.266, as can be seen from comparison of the calculated and measured excitation energies, shown in table 3. Also shown in the table are the results of model potential calculations of the

Table 3. Excitation energies of Rydberg levels converging to the first ionisation potential. The letters a to f in column 1 refer to the peaks labelled in figure 3 and discussed in the text. For levels a to d the measured energies (column 3) are compared with the energies calculated from the Rydberg formula with a quantum defect of 0.266. The final column lists excitation energies calculated by Betts and McKoy (1971).

Level	Present assignment	Excitation Energy (eV)		
		Measured	Calculated from Rydberg formula	Calculated [†]
a	3d(a _{1g})	7.435	7.428	7.238
b	4d(a _{1g})	8.275	8.272	8.238
c	5d(a _{1g})	8.635	8.641	
d	6d(a _{1g})	8.820	8.834	
e	—	7.525		
f	5s(a _{1g})	8.560		8.538

[†] Results of model potential calculations (Betts and McKoy 1971).

energies for Rydberg transitions to the $ns(a_{1g})$ and $nd(a_{1g})$ states by Betts and McKoy (1971). The corresponding quantum defects calculated for the two series were 0.68 and 0.40 respectively, in fair agreement with the values of 0.8 and 0.5 estimated by Jonsson and Lindholm (1969). On the basis of these calculations, the new Rydberg series probably corresponds to the $nd(a_{1g})$ series. The discrepancy of 0.15 eV between the observed position of the 3d(a_{1g}) level and the position calculated by Betts and McKoy (1971) is of the same order as the discrepancy between their results and the experimental positions of the optically-observed states.

The assignment of the strong level f at 8.559 eV cannot be made with confidence. The large quantum defect of 0.56, assuming the convergence limit to be 9.248 eV, would be consistent with its assignment to the 5s(a_{1g}) level, calculated to lie at 8.538 eV by Betts and McKoy (1971), but no evidence for the other members of this series could be found.

The final level, e, is 0.09 eV above level a, and may correspond to an excited vibrational level. This assignment is consistent with the high resolution optical spectra of the R and R' states (Wilkinson 1956) in which progressions in the ν_2 mode were identified, with a similar spacing of 0.086 eV.

4.5. Rydberg states converging to the second ionisation potential

In optical absorption spectra (El-Sayed *et al* 1961, Ockenga *et al* 1979a) two Rydberg series converging to the second ionisation potential of benzene have been detected. These series have quantum defects of 0.28 and 0.47, and appear prominently on the present electron impact spectra (figure 5). The assignment of the transition responsible for these series is not unique. El-Sayed *et al* (1961) suggested that the transitions involve promotion of an electron from the 1 a_{2u}(π -bonding) orbital into the $ns(a_{1g})$ or $nd(a_{1g}, e_{1g})$ Rydberg orbitals, whereas according to Price and Wood (1935) the transitions involve the excitation of a 3e_{2g}(σ -bonding) electron. The latter conclusion was also reached by Ockenga *et al* (1979a), who assigned the Rydberg orbitals as $np(e_{1u})$ and $nf(b_{1u}, b_{2u}$ or $e_{1u})$. No electric dipole-forbidden states have been detected in this energy range.

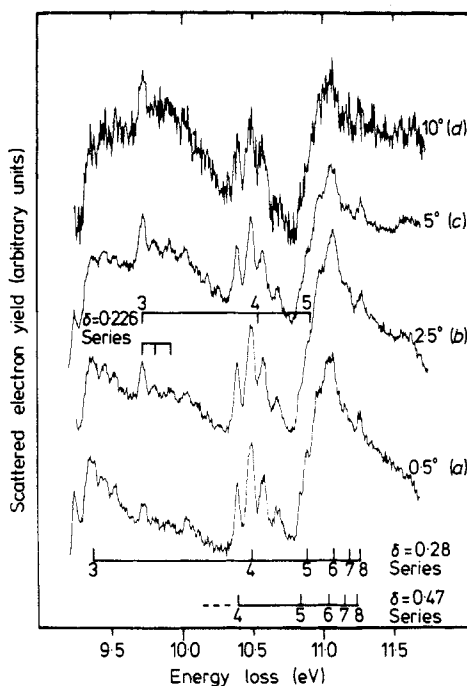


Figure 5. Energy loss spectra showing Rydberg states converging to the second ionisation limit. In each case the scattering angle is indicated beside each spectrum. Two optically-allowed Rydberg series with quantum defects of 0.28 and 0.47 are shown, together with a new series (quantum defect = 0.226) which is discussed in the text.

On the present spectra, a vibrational series of levels, starting at 9.725 eV is observed to increase in intensity as the scattering angle is increased (figures 5(a)–(d)). None of these levels is present on the UV absorption spectra of Ockenga *et al* (1979a). The assignment of the series to a quadrupole state therefore seems certain. Assuming that the ionisation limit to which the new band belongs is also 11.489 eV, the quantum defect for the first level in the band is 0.226. This is very similar to the value of 0.266 for the $nd(a_{1g})$ Rydberg orbital assigned in § 4.4 of the present work. The band at 9.725 eV would thus be assigned to the $3d(a_{1g})$ orbital, and the 4d, and 5d levels would be expected to lie at 10.536 and 10.894 eV, assuming a quantum defect of 0.226. Unfortunately, both energy losses are strongly overlapped by the optically-allowed Rydberg series. The 10.536 eV transition would lie in the dip between two energy-loss peaks, as shown in figure 5. This dip clearly fills in as the scattering angle is increased from 0–5°, consistent with the excitation of an underlying state. In comparison the corresponding dip to lower energy does not show this effect. The 10.894 eV level lies on a sharply-rising background and cannot be distinguished. If the Rydberg orbital is $nd(a_{1g})$, the experimentally-determined fact that the transitions involved are quadrupole-allowed gives an unambiguous assignment of the core electron involved. The transitions $1a_{2u} \rightarrow nd(a_{1g})$ can be excluded since they give rise to states of symmetry $^1A_{2u}$ which are electric dipole-allowed, and quadrupole-forbidden. Conversely, the transition $3e_{2g} \rightarrow nd(a_{1g})$ produces $^1E_{2g}$ states which are electric dipole-forbidden and quadrupole-allowed, and are thus consistent with the present results.

5. Conclusions

Electron impact spectra of the electronic states of benzene having excitation energies up to 11.5 eV have been obtained with a range of excitation conditions. The sensitivity and resolution of the present spectra are much higher than previous electron impact studies of benzene, and many new states have been revealed. Measurements taken at high scattered-electron energies and low scattering angles allow quadrupole-allowed singlet states to be observed, and one such Rydberg series has been found converging to each of the first and second ionisation potentials. The quantum defects of the two series are very similar, and it is suggested that the same Rydberg orbital, $nd(a_{1g})$ is involved in both series. When high scattering angles were used, triplet states were observed with high intensity, and a new triplet band, assigned to the $^3E_{2g}$ state, has been detected for the first time.

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