

LETTER TO THE EDITOR

Absolute elastic electron scattering from benzene

Robert J Gulley and Stephen J Buckman

Atomic and Molecular Physics Laboratories, Research School of Physical Sciences and Engineering, Australian National University, Canberra 0200, ACT, Australia

Received 17 May 1999

Abstract. Absolute measurements of the differential cross section for elastic electron scattering from benzene (C_6H_6) are reported, for the first time, for incident electron energies of 8.5 and 20 eV. The angular distributions are discussed in terms of known negative ion resonance features and a favourable comparison is made with a recent model potential calculation.

Benzene is a molecule of substantial interest for low-energy atomic physics, both from a fundamental and applied point of view. As the simplest aromatic hydrocarbon, and a molecule with a large dipole polarizability and several low-energy negative ion resonances, it provides a challenging but tractable problem for contemporary molecular scattering theory. Benzene is also of interest to astronomy and astrophysics as the polycyclic aromatic hydrocarbons are thought to play an important role in the chemistry of the interstellar medium as mediators of infrared emission bands in the 3–13 μm regions (Leach 1986).

This present work reports the first measurements of absolute differential cross sections for the scattering of electrons from benzene, C_6H_6 . The first experimental measurements of the electron–benzene interaction were published by Holst and Holtsmark (1931) and they described total cross sections at impact energies between 0.5 and 25 eV. Successive investigations on electron interactions with C_6H_6 mainly concentrated on resonant effects, identifying two prominent shape resonances below 10 eV in the process (see Burrow *et al* (1987), who review the experimental and theoretical literature in this field and references therein). The only previous absolute scattering cross sections available in the literature are those of Mozejko *et al* (1996), Sueoka (1988) and Gulley *et al* (1998), all of whom measured the total cross section. The measurements of Mozejko *et al* cover the energy range of 0.6 eV to 3.5 keV, Sueoka measured both electron and positron scattering between 0.7 and 400 eV and Gulley *et al* focused on the very low-energy region between 0.035 and 2 eV. Mozejko *et al* also note a lively interest in electron-impact-induced electronic excitation, as well as other studies concerning electron attachment, dissociative attachment and electron-impact ionization processes. Vibrational excitation in the region of the low-energy shape resonance has also been examined in some detail (see, for example, Wong and Schulz 1975, Cederbaum and Domcke 1976, Gallup 1993 and references therein). Gianturco and Lucchese (1998) have recently published calculations over a broad range of energies (1 meV up to 30 eV) using a parameter-free, exact static-exchange correlation-polarization (SECP) potential to treat the electron–molecule interaction in all scattering symmetries. To our knowledge these are the only contemporary calculations of electron–benzene scattering.

The present measurements were carried out using a crossed-beam apparatus which has been fully described previously (Brunger *et al* 1990, Gulley *et al* 1994) and we do not repeat that detail here. Briefly, the molecular beam is formed by quasi-effusive flow of benzene through a multicapillary array. This beam is crossed with an electron beam, produced by a combination of a thoriated tungsten filament, electrostatic electron optical elements and a hemispherical monochromator. Scattered electrons, either elastic and inelastic, are energy analysed and detected by a further combination of electron optical elements, a hemispherical analyser and a channel electron multiplier, over an angular range between -20° and 130° about the molecular beam axis. The overall energy resolution of the spectrometer for these measurements was typically 50–60 meV and the electron beam current in the interaction region ranged from 0.8 to 3 nA. The absolute electron energy scale is calibrated by observing either the peak in the $N_2^- 2\Pi_g$ resonance at an energy of 2.198 eV for a scattering angle of 60° (Rohr 1977) or the position of the $He^- 1s2s^2 2S$ resonance at 19.367 eV (Brunt *et al* 1977). The absolute cross sections at each energy and scattering angle were determined by use of the relative flow technique (Srivastava *et al* 1975, Nickel *et al* 1989). This technique relies on measurements of the ratio of scattered electron intensities for the gas of interest relative to that for a standard gas. The generally accepted standard cross section is helium and for the present measurements, we have used the elastic differential cross sections of Nesbet (1979) below 20 eV and Brunger *et al* (1992) at 20 eV. The benzene gas was obtained from the saturated vapour above a liquid benzene sample in a glass finger attached to the gas handling system. The liquid sample, of about 50 ml, underwent several freeze–thaw cycles for purification. The vapour pressure above the liquid sample at 20°C was 78 torr.

There are many conditions that need to be fulfilled to properly conduct a relative flow experiment and these have been discussed, in detail, by Gibson *et al* (1999) and references therein. In short, these conditions are related to the magnitude of the driving pressure of each gas behind the beam-forming device. These driving pressures are determined from the mean free paths for each gas, which are calculated, in turn, from published values of their hard-sphere diameters. The relative flow rates of both benzene and helium are then measured for these driving pressures in a separate series of experiments. As has been the case with several other molecules, the literature abounds with differing values for the hard-sphere diameter for benzene. These vary between 5.3 and 7.5 Å and, as a result, the ratio of the driving pressures ($P(\text{He})/P(\text{C}_6\text{H}_6)$) that is required for the scattering experiments varies between 5.9 and 11.7, depending upon one's choice of hard-sphere diameter (a value of 2.19 Å is used for helium). We have investigated the experimental cross sections using driving pressures of 0.1–0.2 torr for benzene and 1.0–1.2 torr for He, corresponding to pressure ratios of 6 to 12, and found no significant effect on the measured absolute cross sections. In order to minimize the effect that gas cycling has on contact potentials and the stability of the electron optical elements, both gases are present in the scattering chamber at all times. This has proved to be particularly beneficial for experiments with benzene as it has a marked effect on the filament emission characteristics.

Of relevance to the present DCS measurements are several negative ion features that have been observed in electron scattering experiments (well summarized, for example, in Burrow *et al* 1987 and Allan 1989) and in the recent calculation of Gianturco and Lucchese (1998). Whilst the bulk of the work in this area has concentrated on the $^2E_{2u}$ and $^2B_{2g}$ states at 1.15 and 4.82 eV, there are also several higher-lying features which overlap the energy range of the present elastic DCS measurements. The total cross section measurements of Mozejko *et al* and Sueoka both show an enhancement at 8–9 eV, as do the excitation functions for vibrational excitation of Azria and Schulz (1975) and Allan (1989). Allan assigned this structure to a σ^* shape resonance which is extremely broad, almost certainly overlapping the lower-energy $^2B_{2g}$

Table 1. Absolute differential cross sections (in units of $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$) for elastic electron scattering from C_6H_6 . The figures in parentheses indicate the absolute uncertainties expressed as a percentage. Integral elastic (Q_e) and elastic momentum transfer (Q_m) cross sections (in units of 10^{-16} cm^2) are given at the foot of each column and the uncertainty in these values is estimated to be $\pm 25\%$.

Angle (degrees)	Incident energy (eV)	
	8.5	20
12	—	49.44 (11.8)
15	26.89 (14.5)	34.82 (8.8)
20	22.90 (8.6)	18.46 (9.4)
25	15.55 (9.5)	9.762 (7.9)
30	10.35 (6.9)	4.390 (9.9)
35	7.421 (8.4)	2.121 (7.7)
40	5.640 (9.3)	1.103 (8.2)
45	4.251 (8.0)	0.707 (8.8)
50	3.305 (8.1)	0.665 (8.6)
55	2.420 (7.5)	0.751 (7.9)
60	1.865 (7.9)	0.826 (8.0)
65	1.675 (7.8)	0.873 (7.6)
70	1.672 (7.2)	0.903 (7.7)
75	1.758 (7.3)	0.866 (8.0)
80	1.828 (7.8)	0.834 (8.5)
85	1.824 (7.0)	0.754 (8.0)
90	1.815 (7.9)	0.715 (9.2)
95	1.703 (7.2)	0.665 (9.3)
100	1.679 (7.3)	0.661 (7.8)
105	1.703 (7.1)	0.674 (9.1)
110	1.720 (8.2)	0.696 (9.9)
115	1.749 (9.0)	0.742 (9.7)
120	1.710 (10.8)	0.832 (11.4)
125	1.590 (10.5)	0.921 (12.9)
130	1.442 (11.6)	1.039 (14.2)
Q_e	45.6	32.4
Q_m	23.1	12.7

resonance. The recent SECP calculations of Gianturco and Lucchese find similar resonance features and assignments, although at slightly higher energies in each case (1.82, 7.5 and 10.1 eV, respectively).

Absolute elastic differential cross sections (DCS) for C_6H_6 have been measured at incident electron energies of 8.5 and 20 eV, and these are presented in table 1. They are also shown in figures 1(a) and (b) where we compare with the recent model potential calculations of Gianturco and Lucchese (1998). At both energies the measured DCS show the same overall trend. At forward angles the scattering is extremely strong, with the interaction being dominated by the long-range polarization effects which result from the large dipole polarizability of the molecule ($\sim 70 \text{ au}$). This strong forward scattering ends abruptly at around 60° and the DCS exhibits oscillatory behaviour at angles out to 130° . In figure 1(a), there is generally good agreement between the experiment and theory (at an energy of 10.1 eV), although the latter is somewhat larger in magnitude at intermediate scattering angles. The comparison with theory is made at this slightly different energy as this is the energy where the broad shape resonance is located in the calculation. Scaling the calculation down by a factor of 1.5 highlights the good shape agreement between experiment and theory and lending further weight to Allan's

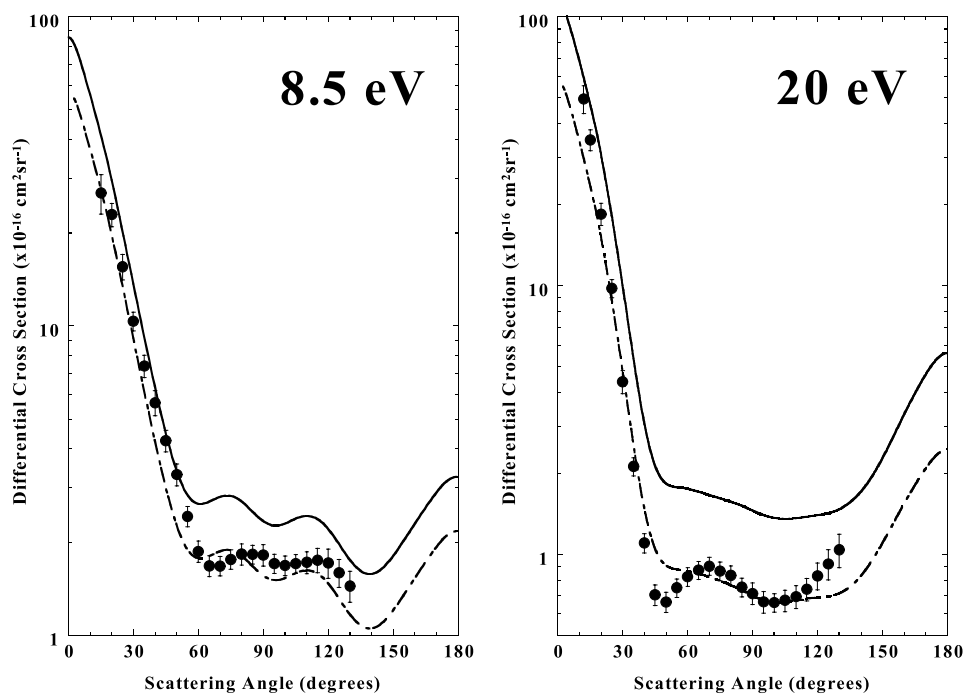


Figure 1. Absolute DCS for elastic scattering from benzene (in units of $10^{-16} \text{ cm}^2 \text{ sr}^{-1}$) at incident electron energies of (a) 8.5 eV and (b) 20 eV. ●, Present results; —, Gianturco and Lucchese; — · —, Gianturco and Lucchese scaled down by a factor of 1.5 and 2.0, respectively.

classification of this feature as a $^2(e_{1u}\sigma^*)$ shape resonance. In figure 1(b) the DCS at 20 eV is in reasonable agreement with the calculation, particularly at forward angles. At larger scattering angles, the experimental DCS demonstrates considerably more structure than the theory and is broadly consistent with an f-wave angular distribution. Once again, the agreement in absolute magnitude between the experiment and theory is improved if the theory is scaled down, in this case by a factor of two.

The present measurements provide an encouraging picture of the level of agreement between theory and experiment for electron scattering from benzene. It is intended to extend these measurements in the near future to both higher and lower energies to further test this agreement, particularly in the region of the two strong, low-energy shape resonances at 1.15 and 4.8 eV.

It is a pleasure to acknowledge the technical skills of Stephen Battison and Kevin Roberts. We are grateful to Professors Franco Gianturco and Robert Lucchese for the provision of tabulated cross section values. RJG acknowledges the support of an Australian Research Council Postdoctoral Fellowship.

References

- Allan M 1989 *J. Electron Spectrosc. Relat. Phenom.* **48** 291
- Azria R and Schulz G J 1975 *J. Chem. Phys.* **62** 573
- Brunger M J, Buckman S J, Allen L J, McCarthy I E and Ratnavelu K 1992 *J. Phys. B: At. Mol. Opt. Phys.* **25** 1823
- Brunger M J, Buckman S J and Newman D S 1990 *Aust. J. Phys.* **43** 665

- Brunt J N H, King G C and Read F H 1977 *J. Phys. B: At. Mol. Phys.* **10** 1289
- Burrow P D, Michejda J A and Jordan K D 1987 *J. Chem. Phys.* **86** 9–24
- Cederbaum L S and Domcke W 1976 *Z. Phys. A* **277** 221–4
- Gallup G A 1993 *J. Chem. Phys.* **99** 827–35
- Gianturco F A and Lucchese R R 1998 *J. Chem. Phys.* **108** 6144–59
- Gibson J C, Green M A, Trantham K W, Buckman S J, Teubner P J O and Brunger M J 1999 *J. Phys. B: At. Mol. Opt. Phys.* **32** 213–33
- Gulley R J, Alle D T, Brennan M J, Brunger M J and Buckman S J 1994 *J. Phys. B: At. Mol. Opt. Phys.* **27** 2593
- Gulley R J, Lunt S L, Ziesel J-P and Field D 1998 *J. Phys. B: At. Mol. Opt. Phys.* **31** 2735–51
- Holst W and Holtsmark J 1931 *K. Nor. Vidensk. Selsk.* **4** 89
- Leach S 1986 *J. Electron Spectrosc.* **41** 427
- Mozejko P, Kasperski G, Szmytkowski C, Karwasz G P, Brusa R S and Zecca A 1996 *Chem. Phys. Lett.* **257** 309–13
- Nesbet R K 1979 *Phys. Rev. A* **20** 58
- Nickel J C, Zetner P W, Shen G and Trajmar S 1989 *J. Phys. E: Sci. Instrum.* **22** 730
- Rohr K 1977 *J. Phys. B: At. Mol. Phys.* **10** 2215
- Srivastava S K, Chutjian A and Trajmar S 1975 *J. Chem. Phys.* **63** 2659
- Sueoka O 1988 *J. Phys. B: At. Mol. Opt. Phys.* **21** L631–5
- Wong S F and Schulz G J 1975 *Phys. Rev. Lett.* **35** 1429