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Absolute total cross section measurements for electron scattering on benzene molecules

Paweł Możejko [a], Grzegorz Kasperski [a], Czesław Szmytkowski [a],
Grzegorz P. Karwasz [b], Roberto S. Brusa [b], Antonio Zecca [b]

[a] *Faculty of Applied Physics and Mathematics, Technical University of Gdańsk, 80-952 Gdańsk, Poland*
[b] *Istituto Nazionale di Fisica della Materia and Dipartimento di Fisica, Università degli Studi di Trento, 38050 Povo, Trento, Italy*

Abstract

The absolute total cross section for electron scattering on C_6H_6 molecules has been measured in two distinct electron-transmission experiments for impact energies between 0.6 eV and 3.5 keV. The present results are compared with other total cross section experimental data.

1. Introduction

Studies concerning the collision of electrons with benzene molecules are quite numerous. However, absolute cross sections in benzene have been measured less frequently than for other molecular targets [1].

The first experimental work on electron–C_6H_6 interactions was performed in the 1930s by Holst and Holtsmark [2], who measured the total cross sections at impact energies between 0.5 and 25 eV using a low-energy Ramsauer technique. Successive intensive investigations of electron scattering from benzene considered mainly resonant effects [3–10]. A lively interest was also devoted to electronic transitions in C_6H_6 [5,11–13] induced by electron collisions. Fewer papers concern electron attachment [14], dissociative excitation [15] and electron-impact ionization processes [16–18].

More recently, Sueoka [19] has determined normalized total cross sections for electron scattering from benzene at energies between 1 and 400 eV, using an apparatus with a relatively strong, longitudinal guiding magnetic field. His results confirmed an intense maximum in the total cross section function at about 8.5 eV, but below this energy the shape of the cross section is quite different from the one obtained by Holst and Holtsmark [2]. In addition to the 8.5 eV maximum, both Holst and Holtsmark's and Sueoka's results show some structures at lower energies. However, whereas in Holst and Holtsmark's measurements a peak is clearly visible at 3.5 eV, in Sueoka's results only a shoulder is barely distinguished at 4.5 eV. Another weak feature around 1.5 eV is present in Sueoka's data, which in turn is not visible in the results of Holst and Holtsmark. Below 1.5 eV the cross section from these two experiments behaves quite differently: it falls down towards lower energies according to Sueoka's data and it rises in the measurements of Holst and Holtsmark.

In the present experiments the absolute total cross section has been measured with an accuracy better

than in the previous work, in a wide energy range from 0.6 to 3500 eV. The measurements below 250 eV were carried out in Gdańsk in a linear transmission mode. From 90 eV to the highest applied energies they were performed with the Ramsauer-type apparatus in Trento. The overlap of the ranges in the two machines allows a cross-validation of the results. Part of our motivation for the present study is to resolve the discrepancies between low-energy data taken in different laboratories [2,19].

2. Experimental

The present total cross section measurements were both made using the electron-transmission method.

In the low-energy experiment (Gdańsk) a linear transmission configuration has been employed. The electron beam was produced with an electron gun and formed by a cylindrical $127°$ electrostatic deflector followed by a system of electron lenses. Energy-selected electrons were sent into a scattering chamber of 30.5 mm length. Those electrons which left the interaction volume through the exit orifice were energetically discriminated with a retarding-field element and then detected by a Faraday cup (solid angle subtended by the detector, averaged over the length L of scattering cell, is 0.7 msr). The total cross section, $\sigma(E)$, at a given energy E was derived by measuring intensities of the electron beam, with (I_p) and without (I_0) the target in the scattering chamber, and applying the Beer–Lambert relationship

$$\sigma(E) = \frac{1}{nL} \ln \frac{I_0(E)}{I_p(E)}. \qquad (1)$$

The absolute number density n of the target gas was determined from absolute measurements of the gas-target pressure and its temperature, taking into account the thermal transpiration effect [20]. In the course of both experiments, the electron optics and the electron source were exposed to a constant background pressure. The energy scale for the impinging electrons was calibrated with reference to the well-known oscillatory resonant structure in nitrogen, around 2.3 eV. In order to lessen the influence of apparatus effects, the measurements were carried out for a given energy in a series of runs using different

sets of electron-beam controlling parameters and a range of target pressures.

In the Trento experiment, the Ramsauer method of measuring both the collector (I_c) and the scattering chamber (I_s) currents was used. The total cross section was obtained from the formula

$$\frac{I_{ci}}{I_{ci} + I_{si}} = \frac{I_{cj}}{I_{cj} + I_{sj}} \exp\left(-\sigma L(n_i - n_j)\right), \qquad (2)$$

where pairs i and j of the currents correspond to two gas densities n_i and n_j, respectively. The use of two current measurements and Eq. (2) allows a better stability. This is essential at high energies where the cathode ion bombardment amplifies any intrinsic instability. The angular resolution of 0.3 msr was achieved by using a two-section [21], 140.2 mm long scattering chamber. The capacitance pressure meter temperature was tracking the scattering chamber temperature within $0.1°C$. Several series of individual measurements have been performed at each energy, an average cross section being calculated for each series. The final values in this Letter are mean and weighted values of these averages.

The overall systematic error does not exceed 7% below 2 eV and 4% elsewhere. Statistical uncertainties (one standard deviation of the mean value) did not exceed 1% in the Gdańsk measurements and 2.5% in the Trento data.

Benzene vapour was obtained from liquid samples of a quoted purity of 99.5% (Aldrich) used without further purification, aside from degassing the liquid with freeze–pump–thaw cycles. More detailed descriptions of the experimental equipment and techniques can be found elsewhere (e.g. [21,22]).

3. Results

Absolute total electron-scattering cross sections for C_6H_6 obtained in both experiments are listed in Table 1 and are shown in Fig. 1 along with the old absolute data of Holst and Holtsmark [2] and the more recent normalized results of Sueoka [19]. No calculations of the $e^- - C_6H_6$ total cross section are available for comparison.

From Fig. 1 one sees that the general character of all the total cross section curves is similar; however,

the present results are higher than the previous data in all the overlapping energy range. At 1 eV the present results are on the average about 10% higher than the results of Holst and Holtsmark [2] and up to 16% above the data of Sueoka [19]. The difference even increases to 20% for energies above 5 eV. For energies above 200 eV the results of Sueoka are about 10% lower than the present data. It is worth noting that for another target (CCl_4), for which total cross sections taken in the same laboratories are available, results of Holst and Holtsmark [2] and Sueoka [23] are lower by more than 30% than those measured in other laboratories [24,25]. This is consistent with the hypothesis of a systematic bias in the previous measurements. The presence of a guiding magnetic field in Sueoka's experiment leads to an uncertainty in the effective length of the interaction region. This is circumvented by Sueoka [23] by normalizing his measured values to the data of Hoffman et al. [26] for e^+–N_2 in the range 25–400 eV. The systematic discrepancy between the present results and those of Holst and Holtsmark [2] could be attributed to a systematic pressure measurement error in their experiment.

The most prominent feature in the cross section is a broad maximum centered near 8.5 eV where the cross section reaches a value of 58×10^{-20} m^2. The existence of this maximum may be in part due to

short-lived resonances observed in this energy region [5,7,12]. We note that similar broad peaks have been observed at 8–10 eV in total and/or integral elastic cross sections in several other hydrocarbons, like CH_4 [27], C_2H_6 [28], and C_3H_8 [29].

Above 1.1 eV, in many works [4,6–9] resonant structures have been observed which correspond [3] to the capture of an incident electron into the doubly degenerate $c_{2u}(\pi^*)$ orbital, yielding the $^2E_{2u}$ electronic state of the benzene anion. The presence of this relatively long-lived weak resonance seems to appear also in the present low-energy experiment as a rather weak structure close to 1.4 eV and in the measurements of Sueoka [19] as a weak hump centered around 1.5 eV. This feature is not visible in the measurements of Holst and Holtsmark [2].

Like Sueoka [19], we did not notice, any satellite maximum at 3.5 eV, which is clearly visible in Holst and Holtsmark's [2] curve. In the same energy range, these latter investigators observed a similar effect also in CH_3Cl [2], which was not confirmed in subsequent experiments [22,30,31]. So one can guess that those structures are an apparatus artifact.

Just below 5 eV a weak shoulder is visible in the present measurements. This shoulder is a small fraction of the total cross section, but has been checked to be perfectly reproducible. This feature, visible also in the data of Sueoka [19], might reflect the
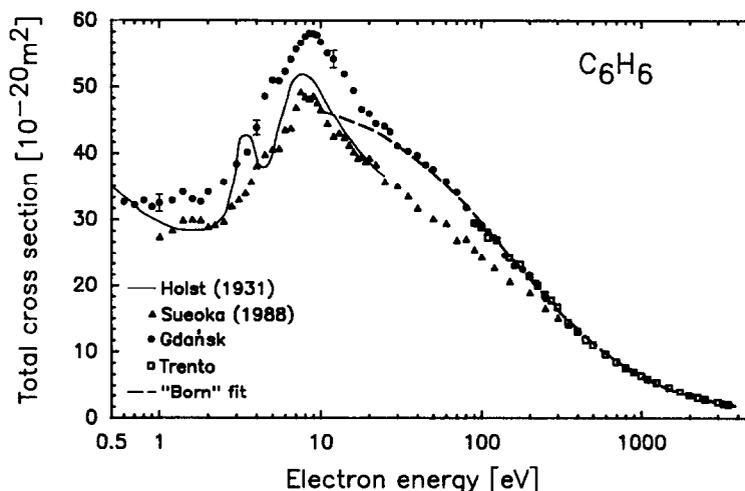

Fig. 1. Total cross sections for electron scattering on benzene molecule. (●) Present measurements (Gdańsk); (□) present measurements (Trento); (△) Sueoka [19]. Solid line: Holst and Holtsmark [2]; dashed line: present intermediate-energy fit, Eq. (3). Error bars in selected points correspond to the total (systematic + statistical) experimental uncertainty. Error bars above 200 eV are smaller than the symbols.

Table 1
Absolute $e^- - C_6H_6$ total cross section (TCS) in units of 10^{-20} m^2. The first and the second TCS columns are results from Gdańsk, the third column are results from Trento

Energy (eV)	TCS	Energy (eV)	TCS	Energy (eV)	TCS
0.6	32.7	20	45.9	90	29.5
0.7	32.2	22	44.4	95	29.4
0.8	32.9	25	44.0	100	28.9
0.9	31.9	27	43.2	110	27.3
1.0	32.5	30	41.1	125	27.0
1.2	32.9	35	40.3	150	24.3
1.4	34.2	40	39.7	175	23.2
1.6	33.1	45	38.3	200	21.4
1.8	32.7	50	37.6	225	20.0
2.0	34.2	60	35.8	250	18.7
2.5	35.7	70	34.1	275	17.8
3.0	38.4	80	31.8	300	16.8
3.5	40.2	90	29.4	350	14.5
4.0	43.8	100	29.2	400	13.4
4.5	48.6	110	28.2	450	12.3
5.0	51.0	120	27.3	500	11.3
5.5	50.9	140	24.6	600	9.71
6.0	52.3	160	23.0	700	8.52
6.5	54.1	180	22.5	800	7.62
7.0	55.6	200	21.6	900	7.05
7.5	56.6	220	20.4	1000	6.47
8.0	57.6	250	18.1	1100	5.96
8.5	58.1			1250	5.47
9.0	58.0			1500	4.67
9.5	57.8			1750	4.01
10.0	56.7			2000	3.50
11.0	55.0			2250	3.07
12.0	54.1			2500	2.83
14.0	51.9			3000	2.38
16.0	49.4			3250	2.18
18.0	46.6			3500	2.04

presence in this energy range of a third short-lived $^2B_{2g}$ resonance observed earlier in electron-transmission spectra [4–7,12].

For energies above 10 eV, the total cross section decreases monotonically with energy. The ionization processes contribute in a substantial way to the total cross section at energies above a few tens of eV. The broad hump visible in the present measurements above 30 eV can probably be attributed to the ionization contribution. The normalized electron-scattering ionization cross sections [16,17], available around 75 eV, constitute about one third of the total cross section. By analogy with other hydrocarbons, one can expect a rising contribution from ionization at

higher energies [32,33]. Absolute measurements of Schram et al. [18] indicate that in C_6H_6 the gross, ionization cross section constitutes at 1000 eV as much as 80% of the total. However, a recent theory [34] indicates that the data of Schram et al. might be overestimated. Only a few experiments have given an absolute scale for particular processes in benzene and therefore the exact determination of a partitioning scheme of the total cross section is a risky task.

The rise of Holst and Holtsmark's [2] curve below 1 eV suggests that the total cross section could exhibit a Ramsauer–Townsend minimum. However, on the basis of the present experiment we can exclude the existence of such a minimum at energies higher than 0.5 eV in benzene. Further experiments at lower energies would be needed.

Between 20 and 3500 eV the total cross section can be approximated reasonably well by a two-parameter formula, used previously for a number of molecules in this energy range [32],

$$\sigma(E) = \frac{\sigma_0}{\left(1 + \sigma_0 \dfrac{E}{B}\right)}. \tag{3}$$

For benzene, the fitting parameters are $\sigma_0 = 50 \times 10^{-20}$ m^2 and $B = 7.4 \times 10^{-20}$ m^2 keV. We note that between 400 and 2000 eV our C_6H_6 total cross section is higher than the C_2H_2 [35] cross section by a factor 2.5.

Acknowledgements

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