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Elastic electron scattering from chlorobenzene

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Abstract

We report a joint theoretical–experimental investigation on elastic electron scattering by chlorobenzene in the low- and intermediate-energy ranges as a part of a collaborative project established between the Federal University of São Carlos (UFSCar) and the California State University (CSUF). More specifically, experimental elastic differential cross sections (DCS), in the incident electron energy range of 1.0 to 800 eV and scattering angle range of 10° to 130°, were measured using the crossed-beam relative-flow technique. Integral and momentum-transfer cross sections were determined from the numerical integration over the experimental DCS. Theoretically, elastic differential, integral, and momentum-transfer cross sections were calculated using a combination of a molecular complex optical potential model with the Padé approximant technique for impact energies ranging from 1.0 to 150 eV. Further calculations of DCS were performed at an energy range of 20 to 500 eV using the independent-atom model. Our results, which significantly extend available electron scattering cross sections for this target, are compared to existing theoretical and experimental data in the literature.

Keywords: electron scattering, cross sections, chlorobenzene

(Some figures may appear in colour only in the online journal)

1. Introduction

In industry, chlorobenzene (C_6H_5Cl) is an important chemical reactant and is used as an intermediate in the production of commodities such as herbicides, dye stuffs, and rubber [1]. Biologically, chlorobenzene and its derivatives are highly toxic. They can inhibit the central nervous system, irritate eyes, affect the upper respiratory system, cause skin sclerosis, and various blood diseases [1, 2] and can even cause cancer. Therefore, such compounds have been ranked as priority (dangerous) pollutants by the United States Environmental Protection Agency and the European Union Environmental Agency [3]. On the other hand, chlorobenzene derivatives (e.g. using nitroand sulfonyl-radicals) can be used as radiosensitizers that are intended to enhance tumor cell killing while having much fewer effects on normal tissues around them because of oxygen transport in tumor cells [4]. This follows the interest in halogenating DNA and RNA bases to make them radiosensitive [5]. In these compounds, low-energy electron attachment has been determined to be key in the dissociation of them to produce active radicals which cause the severing of the DNA and RNA base pair bonds [5]. The destruction of chlorobenzene is important for environmental safety concerns; a method of doing this is using molten salt beds [6]. It would be interesting to see the application of electron driven plasma destruction of chlorobenzene where dissociative electron attachment (DEA) can be applied to break bonds and produce radicals which can be easily adsorbed e.g. regarding the case for destruction of benzene (C_6H_6), using catalysts to enhance dissociation rates, in electron driven non-thermal plasmas [7]. This would be a

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Table 1. Molar masses and dipole moments for selected benzene compounds, arranged in order of increasing mass. Respective dipole moment references are given.

Specie	M(u)	$\mu(D)$	
Benzene	C_6H_6	78.11	0
Toulene	C ₆ H ₅ CH ₃	92.14	0.375 [18]
Benzonitrile	C ₆ H ₅ CN	103.12	4.52 [59]
Xylene-o	$C_{6}H_{5}(CH_{3})_{2}$	106.16	0.45 [19]
Xylene-m	$C_{6}H_{5}(CH_{3})_{2}$	106.16	0.30 [19]
Xylene-p	$C_{6}H_{5}(CH_{3})_{2}$	106.16	0.02 [19]
Chlorobenzene	C ₆ H ₅ Cl	112.56	1.69 [<mark>8</mark>]
Trifluorotoluene	C ₆ H ₅ CF ₃	146.11	2.86 [17]
Hexafluorobenzene	C_6F_6	186.05	0

more dilute form of processing, but nevertheless of industrial interest in industrial exhaust stacks, etc. A discussion of anion resonant-state symmetries associated with resonant DEA to C_6H_5Cl for attachment to the benzene ring and attachment to the C_6H_5-Cl bond is given by Barbosa *et al* [8]. For such applications, it is important to know the energy and scattering angle dependence of electron collisions with this target for modeling studies.

Although electron collisions with chlorobenzene are of importance, there remains a paucity of scattering data for this target. By employing electron transmission spectroscopy, Burrow and co-workers, in several papers, determined the locations of the π^* and σ^* resonances in the DEA of chlorobenzene at incident electron energies (E_0) of 0.75 and 2.44 eV; these values are all summarized by the most recently available work of Modelli and Venuti [9]. In terms of cross section measurements, using a photoionization source of electrons of energy resolution 0.0035 eV, full-width at half maximum, Lunt et al [10] measured very low energy total cross sections for all the halobenzenes. Their total cross sections were taken at incident electron energies (E_0) of 0.015 to 0.650 eV for fluorobenzene (C₆H₅F), 0.24 to 9.9 eV for chlorobenzene, 0.030 to 2.5 eV for bromobenzene (C_6H_5Br), and 0.027 to 9.9 eV for iodobenzene (C_6H_5I). They used a gas cell electron beam attenuation method based on the Lambert-Beer law. They found resonance features in their cross sections at 0.87, 0.75, and 0.69 eV for fluorobenzene, chlorobenzene and bromobenzene, respectively, in excellent agreement with Olthoff et al [11] which is included in the summary of Modelli and Venuti [9] for chlorobenzene. However, Lunt et al [10] did not detect the resonance in iodobenzene around 0.59 eV that was reported in Olthoff et al because of the low pressure of target gas used in their experiment (reduced signal) [10]. A more detailed study of the π^* and σ^* resonances in the DEA of chlorobenzene at incident electron energies (E_0) of 0.75 and 2.44 eV was undertaken by Skalický et al [12] to identify them as temporary electron captures at 0.84 to 1.4 eV (lower energy resonance) to the b_1 and $a_2\pi^*$ orbitals with the broader band peaking at 2.6 eV appears in the excitation of the C-Cl stretch vibration corresponding to temporary electron capture in the $\sigma^*_{\rm C-Cl}$ orbital, not in the benzene ring as it was earlier suggested. Total cross sections (TCS) for electron scattering from benzene and chlorobenzene have been measured, using the linear

2

transmission time-of-flight method, by Makochekanwa et al [13] for E_0 values from 0.4 to 1000 eV. They observed resonance structures at 0.8 and 2.5 eV and which merge to the single resonance at 1.6 eV of the benzene molecule. They claim this to be evidence of the splitting of the degenerate e_{2u} orbital of the benzene molecule into two, upon substitution of an H atom in the benzene by the Cl atom to give chlorobenzene. A very recent theoretical study of e⁻-chlorobenzene scattering data on resonances, differential cross-sections (DCS), momentum transfer cross-sections (MTCS), rate coefficient, vertical electronic excitations, dissociative electron attachment, total ionization cross-sections, and TCS was undertaken by Prajapati et al [14] using the R-matrix approach for molecules. Unfortunately, they did not identify the 0.75 or 2.44 eV resonances in their theory although they compile a useful overall table of resonances at other energies.

The first experimental electron scattering DCSs and a detailed theoretical study of elastic scattering resonances of chlorobenzene was made by Barbosa *et al* [8]. Their experimental work was undertaken at E_0 values of 8 eV and above, so they could not empirically detect resonant structures which lay below 8 eV, but from their theoretical studies using the Schwinger multichannel with pseudopotentials (SMCPP) method, they identified resonances characterized as π^* at around 0.7, 0.76, and 5.2 eV belonging respectively to the B₁, A₂, and B₁ symmetries and a σ^* resonance at 2.8 eV of A₁ symmetry, in agreement with most of the literature published. Their experimental relative elastic electron scattering DCSs were taken at E_0 values of 8, 10, 20, 30, and 50 eV for electron scattering angles (θ) of 7° to 110° and placed on an absolute scale using the SMCPP theoretical results.

Elastic electron scattering from benzene or benzene-related compounds were first those of benzene by Gulley and Buckman [15] at E_0 of 8.5 eV and 20 eV which were followed by more extensive measurements of Cho *et al* [16] at E_0 values of 1.1 eV to 40 eV and θ values of 20° to 130°. The latter work included similar measurements for hexachlorobenzene (C_6Cl_6) at E_0 values of 1.5 eV to 100 eV and similar θ values. Kato et al [17] measured DCSs for electron scattering from toluene ($C_6H_5CH_3$) and trifluorotoluene ($C_6H_5CF_3$) at E_0 values of 1.5 eV to 200 eV and θ values of 15° to 130°. In their results, the two molecules show similar magnitudes and shapes of the DCSs at intermediate to high E_0 values of 7 eV to 200 eV and the DCSs for trifluorotoluene increase more steeply than toluene θ due to its higher dipole moment over toluene (see table 1) at lower E_0 and θ values as should be expected. Their DCSs for the dipole-active toluene and trifluorotoluene molecules confirm the evidence of a d-wave resonant angular distribution in the vibrational excitation; additionally, the overall dominance of the benzene ring molecular structure in the collision dynamics is observed as is expected. Later work by our group for toluene by Sakaamini et al [18] showed good agreement with those of Kato *et al* [17] except at the lowest E_0 of 1.5 eV where we see a stronger dipole forward-scattering in significantly better agreement with the SMC theory [18]. Our group has also measured low energy elastic scattering for the ortho-, meta, and para-isomers of xylene $(C_6H_4(CH_3)_2)$ [19]

Table 2. Experimental DCS (in 10^{-16} cm²/sr), ICS and MTCS (in 10^{-16} cm²) from the CSUF experiment for elastic electron scattering from chlorobenzene.

Angle	1 eV	Error	2 eV	Error	2.42 eV	Error	3 eV	Error	4.39 eV	Error	5 eV	En	ror	
15							9.99	1.39	23.57	3.26	25.68	3	3.59	
20	12.7	1.72	14.92	2.20	12.16	1.68	8.90	1.17	14.66	1.95	18.00	18.00 2.31		
25	9.62	1.18	10.30	1.30	7.86	1.04	7.14	0.91	11.08	1.43	13.55	13.55 1.78		
30	7.93	1.04	6.65	0.80	6.30	0.80	6.17	0.79	8.20	1.02	10.17	10.17 1.2		
40	4.34	0.53	4.48	0.57	4.30	0.55	4.99	0.64	6.34	0.81	7.57	7.57 0.93		
50	2.90	0.39	4.10	0.51	3.84	0.51	4.69	0.58	5.65	0.71	6.02	6.02 0.7		
60	2.75	0.37	4.32	0.55	3.59	0.45	3.70	0.48	4.39	0.56	4.52 (.57	
70	2.90	0.38	4.23	0.54	3.41	0.43	2.95	0.39	3.61	0.47	3.55 (.47	
80	3.21	0.40	3.68	0.46	2.69	0.36	2.67	0.36	2.89	0.35	2.74 0.3		.35	
90	3.87	0.49	2.97	0.37	2.40	0.32	2.41	0.30	2.44	0.31	2.63	0	.34	
100	3.76	0.47	2.54	0.31	2.04	0.27	2.38	0.30	2.26	0.28	2.70	0	.34	
110	3.71	0.51	2.28	0.29	2.10	0.28	2.25	0.30	2.62	0.34	2.69	0	.36	
120	3.52	0.47	2.12	0.27	2.53	0.32	2.45	0.32	2.70	0.34	2.89	0	.37	
130	4.12	0.58	2.35	0.29	2.59	0.35	2.52	0.31	2.79	0.37	2.96	0	.37	
ICS	55.54	7.63	53.21	8.66	49.11	9.14	44.38	6.12	56.59	7.85	61.83	8	.56	
MTCS	51.15	7.61	40.27	7.42	38.97	7.74	36.56	5.71	41.15	6.54	43.68	6	.91	
Angle	8 eV	Error	10 eV	Error	15 eV	Error	20 eV	/ En	or 30 e	eV Ei	rror 50) eV	Error	
10			74.04	9.97	62.32	10.07	79.56	5 10.	98 49.2	23 7.	.73 64	1.86	9.95	
15	39.72	5.87	49.46	6.52	44.99	6.14	47.76	6.4	40 27.	32 3.	.75 23	3.72	3.31	
20	27.34	3.61	33.29	4.49	26.28	3.45	23.50	2.9	98 12.	95 1.	.68 6	.93	0.92	
25	16.37	2.12	22.04	2.98	17.43	2.20	14.38	8 1.8	6.1	2 0	.77 2	.55	0.35	
30	11.82	1.52	14.65	1.96	11.07	1.41	8.26	1.(05 3.5	0.7	.45 1	.48	0.19	
40	6.19	0.78	7.00	0.91	4.67	0.64	3.72	0.4	47 1.7	2 0.	.22 0	.70	0.09	
50	4.56	0.59	4.65	0.63	3.39	0.43	2.21	0.2	28 0.9	0.0	.11 0	.50	0.06	
60	3.35	0.41	3.32	0.45	2.22	0.28	1.78	0.2	0.6	0 0	.08 0	.31	0.04	
70	2.86	0.37	2.84	0.37	1.72	0.22	1.28	0.1	17 0.3	9 0.	.05 0	.15	0.03	
80	3.12	0.40	2.75	0.35	1.40	0.18	0.96	0.1	12 0.3	4 0	.04 0	.19	0.02	
90	2.63	0.34	2.45	0.31	1.30	0.17	0.88	0.1	11 0.3	6 0	.05 0	.18	0.02	
100	2.70	0.34	2.71	0.35	1.37	0.18	0.98	0.1	12 0.3	4 0	.04 0	.23	0.03	
110	2.93	0.37	2.69	0.35	1.55	0.20	1.05	0.1	13 0.4	2 0	.05 0	.26	0.03	
120	2.81	0.36	2.58	0.33	1.70	0.22	1.23	0.1	15 0.4	1 0	.05 0	.25	0.03	
130	2.50	0.33	2.61	0.33	1.93	0.26	1.39	0.1	18 0.5	4 0	.07 0	.23	0.03	
ICS	63.48	8.51	73.07	11.27	54.16	7.48	49.43	3 7.2	24 25.5	51 4	.27 23	3.39	5.70	
MTCS	37.16	4.80	36.40	4.76	24.88	3.41	19.12	2. 3.0	05 7.8	8 1	.55 5	.70	0.94	

and find the DCSs of these isomers to be essentially very similar, but about a factor of two higher in magnitude than toluene, importantly showing the significance of the extra-CH₃ groups which were attached to the benzene ring to form toluene into xylene [19]. Our group has also measured elastic scattering from benzonitrile (C₆H₅CN), which has a nitrile (C \equiv N) radical attached to the benzene ring [20], at similar low E₀ values. These data are to be published later in full will be partially compared to the present work on chlorobenzene plus benzene ring related compounds existing in the literature (see table 1).

In the present work, we present a large body of elastic scattering DCSs for chlorobenzene for twelve E_0 values from 1 eV to 50 eV (CSUF group) and nine E_0 values from 20 eV to 800 eV (UFSCar group), with overlapping E_0 values between the two data sets at 20 eV, 30 eV and 50 eV as a check of continuity of the results of the separate setups. The relative flow technique [21] (RFT) is used in both experiments except He is used as a standard gas in the CSUF system whereas N₂ and Ar gases are used in the UFSCar system. Also, at energies ranging from 1 to 150 eV, calculations were performed using a molecular complex optical potential (MCOP) where the scattering equations were solved using a single-center expansion technique combined with Padé approximant [22–24]. Further cross sections calculations were made in the 20–500 eV range using the independent atom model (IAM). The results are compared with the experimental data and the SMCPP theoretical results of Barbosa *et al* [8]. The results are also compared to existing experimental DCSs for similar benzene related targets discussed above to relate the importance of the benzene group in the collision dynamics.

In section 2 we describe both the experimental setups and procedures of the CSUF and UFSCar experiments and, in section 3 we describe the present theoretical procedure. In section 4 we compare and discuss the present measured and theoretical results, along with previous data reported in the literature. Finally in section 5 we draw some conclusions about this work as it appertains to chlorobenzene and benzene-type molecules.

Table 3. Experimental DCS (in 10^{-16} cm²/sr), ICS and MTCS (in 10^{-16} cm²) from the UFSCar experiment for elastic electron scattering from chlorobenzene.

Angle	20 eV	Error	30 eV	Error	50 eV	Error	100 eV	Error	150 eV	Error
15			24.1	4.1	8.85	1.86	8.17	0.90	4.85	0.53
20			11.4	1.9	3.42	0.72	2.74	0.30	1.89	0.21
25	14.8	2.5	4.62	0.78	2.20	0.46	1.85	0.20	1.40	0.15
30	7.81	1.32	2.63	0.45	1.37	0.29	1.22	0.13	0.933	0.103
35	4.71	0.80	1.75	0.30	0.987	0.207				
40	2.97	0.50	1.22	0.21	0.879	0.185	0.468	0.051	0.444	0.049
45							0.350	0.039	0.394	0.043
50	1.57	0.27	0.763	0.130	0.501	0.105	0.303	0.033	0.374	0.041
60	1.18	0.20	0.646	0.110	0.233	0.049	0.304	0.033	0.214	0.024
70	0.983	0.167	0.448	0.076	0.196	0.041	0.194	0.021	0.140	0.015
80	0.814	0.138	0.405	0.069	0.221	0.046	0.134	0.015	0.118	0.013
90	0.721	0.123	0.432	0.073	0.231	0.049	0.134	0.015	0.108	0.012
100	0.768	0.131	0.455	0.077	0.227	0.048	0.121	0.013	0.087	0.010
110	0.685	0.116	0.435	0.074	0.204	0.043	0.124	0.014	0.087	0.010
120							0.136	0.015	0.095	0.010
130							0.180	0.020	0.109	0.012
ICS	46.9	14.1	29.5	8.9	17.2	5.2	12.4	3.7	8.6	0.3
MTCS	15.8	4.7	8.4	2.5	5.0	1.5	3.8	1.1	2.4	0.1
Angle	200 eV	Error	300 eV	Error	400 eV	Error	500 eV	Error	800 eV	Error
15	5.34	0.59	5.23	0.57	4.87	0.54	2.77	0.30	2.67	0.45
20	2.74	0.30	2.44	0.29	1.82	0.20	1.38	0.15	1.76	0.30
25	1.72	0.19	1.24	0.14	1.31	0.14				
30	0.917	0.101	1.10	0.12	1.05	0.12	0.805	0.089	0.563	0.096
40	0.733	0.081	0.575	0.063	0.383	0.042	0.339	0.037	0.258	0.044
45	0.587	0.065	0.396	0.044	0.307	0.034				
50	0.393	0.043	0.288	0.032	0.249	0.027	0.199	0.022	0.139	0.024
60	0.252	0.028	0.205	0.023	0.179	0.020	0.115	0.013	0.088	0.015
70	0.189	0.021	0.144	0.016	0.108	0.012	0.075	0.008	0.056	0.010
80	0.141	0.016	0.092	0.010	0.076	0.008	0.053	0.006	0.044	0.007
90	0.129	0.014	0.071	0.008	0.070	0.008	0.044	0.005	0.034	0.006
100	0.100	0.011	0.069	0.008	0.060	0.007	0.036	0.004	0.024	0.004
110	0.085	0.009	0.080	0.009	0.052	0.006	0.032	0.004	0.021	0.004
120	0.101	0.011	0.096	0.011	0.047	0.005	0.029	0.003	0.019	0.003
130	0.122	0.013	0.096	0.011	0.051	0.006	0.027	0.003	0.019	0.003
ICS	6.6	2.0	5.9	1.8	4.4	1.3	3.2	1.0	2.6	0.8
MTCS	2.1	0.6	1.6	0.5	1.1	0.3	0.7	0.2	0.4	0.1

2. Experimental method

2.1. Low energy CSUF experiment

The CSUF experimental setup has been detailed elsewhere in e.g. Khakoo *et al* [25] so only a brief description is given here. It used a well-tested electron spectrometer employing double hemispherical energy selectors made of titanium in both the electron gun and detector. Several sets of 2.5 cm diameter cylindrical lenses were used to transport electrons through the spectrometer; which was baked to about 80°C to 130°C with magnetically-free bi-axial heaters [26] to keep the spectrometer surfaces stable in the experiment for operation for periods of 4+ months. Electrons were detected by a discrete dynode electron multiplier [27] with a dark count rate of <0.01 Hz and capable of linearly detecting >10⁵ Hz without saturating. The remnant magnetic field was reduced to ≈1 mG in the collision region by insertion of a double μ -metal shield. The standard electron current ranged from 18–25 nA, with an energy resolution of 40-70 meV, full-width at half-maximum. Lower currents were chosen for lower E_0 values to minimize space charge broadening of the incident electron beam. The electron beam could be focused at 0.5 eV and remained stable, varying less than 15% at maximum during the data acquisition period. The energy of the beam was established by measuring the minimum in the elastic scattering of the 2²S He-resonance at 19.366 eV [28] at the θ of 90° to \approx 45 meV stability during a daily run. The contact potential varied between 0.60 eV to 0.70 eV. The elastic peaks of the energy loss spectra were collected at fixed E_0 and θ values by repetitive multi-channelscaling techniques. The effusive target gas beam was formed by flowing gas through a ≈ 0.4 mm diameter thin aperture (≈ 0.025 mm thick), which was sooted (using an acetylene flame, as were the spectrometer collision region surfaces) to reduce secondary electrons. The usage of an aperture source instead of a tube gas collimator removes the need to maintain the backing pressures of target gases in an inverse ratio of their molecular diameters (in order to equalize the mean free path of the two target gases [29] in the gas collimating structure), see e.g. [29]; for the thin aperture, the mean free path is always greater than the thickness of the aperture, resulting in a fixed $\cos \theta$ profile of the gases uses [30]. This is advantageous when working with heavy molecular targets with masses around 100 u (such as chlorobenzene) as determining the uncertainty in the gas kinetic molecular diameters can be considerable and applying the inverse molecular diameter gas pressure ratio accurately in the RFT at moderate or high target source pressures, is made more challenging with controlling the stability in the flow of these viscous mass targets through collimating needle sources. The aperture, located ≈ 6 mm below the axis of the electron beam, was incorporated into a movable source [29, 31] arrangement which moved the aperture into and out of alignment with the incident electron beam at the collision region center. The moveable gas source method determined background electron-gas scattering rates expediently and accurately [29]. The measured DCSs were normalized using the RFT with helium as the reference gas. The pressures behind the aperture were measured by an absolute capacitance manometer [32], and ranged from 1.2 to 1.8 Torr for He and 0.15 to 0.22 Torr for chlorobenzene, resulting in a chamber pressure ranging from 8×10^{-7} Torr to 1.8×10^{-6} Torr. The chlorobenzene liquid was obtained from Sigma–Aldrich with a \geq 99.8% purity. The liquid was placed in a 50 c.c. all glass-metal flask attached by baked 1/4-inch refrigeration copper tubing to the experimental gas handling system, which was also heated by the same bi-axial heaters as above. The liquid sample was purified from dissolved gases by liquid N₂ freeze-pump cycles. Chlorobenzene has a large molecular mass (112.56 u), resulting in increased viscosity, which initially caused periodic instabilities in the flow as it partially choked up our gas metering valve [33]. To counter this, the valve and the entire gas line afterwards was baked at a temperature of about $\approx 80^{\circ}$ C to 100° to counter-act this valve choking problem by preventing condensation of chlorobenzene in the valve and gas lines. Each DCS was taken a minimum of two times in a run to check its reproducibility and a weighted average was made of multiple data runs to obtain the final DCSs. In this experiment, there was no need to separately normalize the chlorobenzene DCSs obtained, as the profiles of the unknown and standard target gases were the same. However, it was possible to determine the stability of the experimental from separate full θ runs of He followed by chlorobenzene (or vice-versa) at any fixed E_0 . This is different from the UFSCar system described next.

2.2. Intermediate energy UFSCar experiment

Two experimental setups at UFSCar were used to perform the DCS measurements. Both spectrometers were described elsewhere [34–37] and will be briefly presented here. The measurements at energies below 100 eV were performed using a spectrometer [37] that employs a commercial electron source (Comstock EG-451) composed of an electron gun and a spherical sector electrostatic energy monochromator of a 36.5 mm mean radius with entrance and exit apertures of 1.0 mm and 0.5 mm diameters, respectively. A set of cylindrical lenses

were used to transport and focus the electrons to the collision region. The energy of the scattered electrons was analyzed by the same size spherical sector and detected by microchannel plates. A three-element cylindrical lens was used to control the pass energy and focus the scattered electrons at the entrance of the analyzer. Both spherical sectors and the transport lenses are made of OFHC copper. The analyzer can be rotated from -10° to 110° with respect to the incident beam and all surfaces exposed to the electron beam path were coated with colloidal graphite to reduce secondary scattering. A layer of μ -metal shielding lines the interior of the chamber, reducing the magnetic field to less than 3 mG. The measurements were performed with a $\Delta E \approx 180$ meV (full-width at half maximum) and currents in the range of 0.5–2 nA.

The spectrometer used for the measurements at 100 eV and above has a non-monochrome electron gun that yields a beam with a thermal $\Delta E \approx 0.5$ eV and currents in the range of 50–150 nA. The energy of the scattered electrons was analyzed by a retarding-field analyzer located in front of the detector (channeltron) with an energy window of about 1.5 eV. The measurements were performed in the angular range of 10°–130° and the magnetic field in the collision region was reduced to around 15 mG using three perpendicular Helmholtz-based coils.

In both spectrometers, the gas beam was produced using a molybdenum tube with an internal diameter of 1 mm and a diameter-to-length aspect ratio of $\gamma = 0.03$. The gaseous samples were generated from the saturated vapor above the chlorobenzene liquid (Sigma-Aldrich, $\geq 99.8\%$ purity) in a small vial attached to the gas handling system [38]. Several cycles of freeze-pump-thaw degassing were performed to eliminate atmospheric air and other volatile contaminants. Periodically, the presence of contaminants was checked using a quadrupole mass analyzer and was found to be negligible. The base pressure in the first spectrometer above described was 2×10^{-8} Torr whereas in the second one was around 1×10^{-7} Torr. The working pressures were in the range of $\approx 1-2 \times 10^{-7}$ Torr and $\approx 0.5-2 \times 10^{-6}$ Torr, respectively.

For each incident electron energy, the relative angular distribution of the scattered electrons was measured at least three times to verify its reproducibility. These angular distributions were converted to absolute DCSs using the RFT where the intensities of electrons scattered by chlorobenzene were compared to a reference gas in the same setups. The experimental elastic DCSs of N_2 [39] and Ar [40, 41] were used to normalize our data in the 20–50 eV and 100–800 eV range, respectively. The relative flow rates were obtained by the procedure described in prior works [34, 38]. The sample driving pressures, measured by an absolute capacitance manometer, were kept lower than 0.2 and 0.5 Torr, for chlorobenzene and reference gases, respectively.

2.3. Comparison of CSUF and UFSCar RFT applications

The RFT [21] was employed in both experiments to determine normalized elastic electron scattering DCSs for chlorobenzene. However, its application in the two experiments was different and needs to be elaborated; this is important since the CSUF experiment used an aperture collimator of gas whereas



Figure 1. DCS for elastic scattering from chlorobenzene at $E_0 = 1, 2, 3, 5, 8$ and 10 eV. Experiment: (•) CSUF data; (•) Barbosa *et al* [8]; theory: (- -) SMCPP SEP calculation [8]; (----) MCOP SEP calculation.

the UFSCar experiment used a tube collimator and the two were systematically different in design. So agreement between the two experiments is to be favorably considered not due to systematic setups in the apparatus.

In the CSUF system, the standard gas A (He) and the unknown gas (X = chlorobenzene) were flown separately at drive pressures behind the source of gas P_A and P_X from which the relative gas flow rate RFR_A and RFR_X (s⁻¹) were determined during the experiment as a quadratic function of the driving pressure (e.g. for X) as:

$$RFR_X = aP_X + bP_X^2, \tag{1}$$

where the coefficients *a* and *b* were determined in a separate experiment prior to the cross section measurement (for details see Khakoo *et al* [29]). The DCS for *X* can then be determined

from comparison with A at the same E_0 and θ as:

$$DCS(E_0,\theta)_X = DCS(E_0,\theta)_A \frac{RFR_A}{RFR_X} \frac{I_{e_A}}{I_{e_X}} \frac{I_{S_X}}{I_{S_A}} \sqrt{\frac{M_A}{M_X}}, \quad (2)$$

where the I_S is the elastic scattered electron rate, I_e is the incident electron current which is found to be reliably applicable only if the current remained within 10% stability, and M are the molar masses. In the CSUF experiment, this equation can be used for a range of flow rates for X and A and, was usually used at moderate flow rates to get adequate signal rates.

In the UFSCar, the experiments were performed to yield relative angular scattering distributions at constant pressures for the chlorobenzene. After that accurate normalized DCS(E_0 , θ)_X were obtained applying the RFT at one θ . For that, the RFR for both chlorobenzene and standard



Figure 2. DCS for elastic scattering from chlorobenzene at $E_0 = 20$, 30, 50, and 100 eV. Experiment: (•) CSUF data; (•) UFSCar data; (•) Barbosa *et al* [8]; theory: (- - -) SMCPP SEP calculation [8]; (----) MCOP SEPA calculation; (----) IAM SEPA results.

gases was obtained following the technique of the pressure decrease [38] performed before the cross-section measurements. Although the quadratic behavior given by equation (1) has been observed, in the current work, the normalization procedure was performed in a lower-pressure regime (P < 0.3 Torr), so the mean-free path of the atoms/molecules was comparable or greater than the collimating gas tube diameter. In such a low-pressure condition the second-order contribution in equation (1) was made negligible and the DCS for the chlorobenzene can then be determined as [21]

$$DCS(E_0,\theta)_X = DCS(E_0,\theta)_A \frac{P_A}{P_X} \frac{I_{e_A}}{I_{e_X}} \frac{I_{S_X}}{I_{S_A}}.$$
 (3)

Importantly, we note here that the CSUF experiment used He as a standard, with its DCS from the well-established work of Nesbet [42] for $E_0 < 20$ eV and of Register *et al* [43] for $E_0 \ge 20$ eV. On the other hand, the UFSCar experiment used N₂ as the standard gas for $E_0 < 100$ eV, using the well-known cross sections of Shyn and Carignan [39], and Ar as standard gas for $E_0 \ge 100$ eV using the cross sections of Jansen [40] and Dubois and Rudd [41].

2.4. Integral cross sections

The experimental ICSs and MTCSs were obtained by extrapolating the DCSs to $\theta \approx 0^{\circ}$ and to 180° and then integrating the DCSs as e.g. described in previous work [18, 19, 44]. Since chlorobenzene is a polar molecule, the long-range interaction due to the molecular dipole moment gives rise to a steep variation of the DCS in the region of small scattering angles which are not covered by the experiments making the extrapolation procedure essentially arbitrary [45]. Consequently, for all the low E_0 CSUF data, the Born-dipole formula [46] (with an inelastic-scattering energy-loss value of 5 meV, this reasonably representative of rotational excitation within the elastic scattering energy-loss peak [44]) was employed to extrapolate the DCSs to small θ . This extrapolation circumvents the singularity of the purely elastic Born-dipole DCSs $\rightarrow \infty$ as $\theta \rightarrow 0^{\circ}$ and thus obtains realistically finite ICSs. Fortunately, the sin θ term in the ICS integral also helps to suppress the singularity as $\theta \to 0^\circ$ leading to significantly reduced extrapolation errors. For the higher E_0 energies of the UFSCar data, the shapes of the MCOP DCS curves were used as a reference to extend the data from 20 to 150 eV to near the forward and backward directions. Above 200 eV, the extrapolations were carried out following the IAM trends at high angles, and at the forward direction, the extrapolations were carried out manually [35].

2.5. Error analysis

The experimental uncertainties in the current data are similar to those for previously reported data [36, 37]. Briefly, typical uncertainties in the DCSs include statistical scattered electron count errors (1 to 6%), uncertainty in the flow rate (3%), the



Figure 3. DCS for elastic scattering from chlorobenzene at $E_0 = 150, 200, 300, \text{ and } 500 \text{ eV}$. Experiment: (**I**) UFSCar data. Theory: (-----) MCOP SEPA calculation; (------) IAM SEPA results.



Figure 4. Electron scattering for chlorobenzene at $\theta = 90^{\circ}$. (•) DCSs from table 1; (-----) experimental excitation function.

variation of the incident electron current (5%), and the standard deviation error on the reproducibility of the DCSs from different data runs. In the CSUF experiment, these errors combined with the quoted errors for the reference gas provide an overall experimental uncertainty in the absolute DCS of around 13% whereas in the UFSCar experiment the overall uncertainties are around 17% at 20, 30, and 800 eV, 21% at 50 eV, and 11% at other energies. The evaluation of the ICSs by extrapolation of DCSs to extreme angles incurs an additional error of \approx 10 to 15%.

3. Theory and numerical procedure

3.1. Molecular complex optical potential

Following the procedure detailed in previous studies [24, 36, 37, 47] a molecular complex optical potential (MCOP) represented by

$$V_{\rm opt} = V_{\rm st} + V_{\rm ex} + V_{\rm cp} + iV_{\rm ab} \tag{4}$$

was used to describe the e⁻-chlorobenzene interaction at the static-exchange-polarization-absorption (SEPA) level of approximation. Using this potential, the many-body nature of the interaction potential was reduced to a one-particle scattering problem. Briefly, the real part of equation (4) depicts the static, exchange, and correlation-polarization interaction potentials, respectively, while the complex part takes account for the absorption contribution. The V_{st} and V_{ex} were obtained from a near-Hartree-Fock self-consistent-field (HF-SCF) molecular wave function and the V_{cp} was obtained from a parameter-free local density model of Perdew and Zunger [48]. The V_{ab} was described in the framework of the scaled quasi-free scattering model (SQFSM) potential of Lee et al [49]. A single-center-expansion about the center of mass of the molecule was applied in terms of symmetry-adapted functions to the molecular wave function and interaction potentials [50], and the scattering equations were solved iteratively by the



Figure 5. Experimental DCSs for elastic scattering from several benzene related compounds (a) all at $E_0 = 15$ eV, (b) all at $E_0 = 30$ eV, except toluene at $E_0 = 20$ eV. (**n**) Cho *et al* [16]; (**a**) Sakaamini *et al* [18]; (**•**) Khakoo *et al* [20]; (**•**) Sakaamini *et al* [19]; (**•**) present work; (\diamond) Kato *et al* [17]; (**□**) Cho *et al* [16].

[N/N] Padé's approximant technique using the e-PolyScat-D package [22–24]. After the convergence tests, 40 partial waves were used for all bound and continuous orbital expansions. For the T-matrix elements, 20 partial waves were used for the calculations below 50 eV and 30 partial waves above.

The HF-SCF ground-state wave function for the chlorobenzene was obtained using the cc-pVTZ basis set of the Gaussian 09 [51]. For that, the experimental molecular geometry [52] was used. This provided a total energy of -689.72 a.u. and an electric dipole moment of 1.86 D, which overestimates the experimental value of 1.69 D [53]. To generate the asymptotic part of the correlation-polarization potential, the dipole polarizabilities $\alpha_{xx} = 43.241$ a.u., $\alpha_{yy} = 80.368$ a.u., and $\alpha_{zz} =$ 101.798 a.u. determined from the HF-SCF calculation, were used. The experimental ionization energy (11.861 eV) [52] was taken into account for generating the absorption potential. In the computations, the C_{2v} point group was used to describe the symmetry of the chlorobenzene.

Due to the non-zero permanent dipole moment of chlorobenzene, a procedure based on the Born-closure formula was used to account for the high partial-waves contributions to the scattering amplitudes. For details of the Born-closure procedure see e.g. Hlousek *et al* [37].

3.2. Independent atom model

DCS calculations were also performed within the IAM framework [54] at the SEPA level of approximation [34] for energies from 20 to 500 eV. For that, the V_{st} reported by Salvat *et al* [55], the V_{ex} proposed by Furness and McCarthy [56], and the V_{cp} of Perdew and Zunger [48] were used. The potential model to account for the V_{ab} contributions was also the SQFSM potential of Lee *et al* [49]. The molecular geometry and all other parameters, like atomic polarizabilities and atomic mean excitation energy (considered to be the first ionization energy) used in the calculations were taken from the literature [52, 57]. Also, the IAM additivity rule (AR) [54] was used to obtain the ICS at the 10–1000 eV energy range.

4. Results and discussion

4.1. Differential cross sections

Our chlorobenzene DCSs, ICSs, and MTCSs are tabulated in table 2 (CSUF results) and table 3 (UFSCar results) along with their corresponding uncertainties (1 standard deviation). The low energy DCSs for E_0 from 1 eV to 10 eV are shown in figure 1 and for E_0 from 20 eV to 100 eV in figure 2. The DCSs for E_0 from 150 eV to 500 eV are shown in figure 3. Typical forward peaking is exhibited at low E_0 because of the permanent dipole moment of chlorobenzene of 1.69 D [53]. In figure 1, the agreement between our experimental results and those of Barbosa *et al* [8] at 8 and 10 eV is excellent. At E_0 of 1 to 3 eV, our MCOP SEP calculation shows significantly larger DCSs at small angles ($\theta \leq 40^{\circ}$) but improves markedly for $E_0 \ge 5$ eV with an excellent agreement at 10 eV. The SMCPP SEP results of Barbosa et al also show excellent agreement with the experiment at $E_0 \ge 3$ eV. At E_0 of 10 eV both our experimental results and those of Barbosa et al [8] as well as their SMCPP SEP calculation and our MCOP calculation are in excellent agreement.

In figure 2, at E_0 of 20 eV, which constitutes the overlap E_0 of the CSUF and UFSCar experimental data, the experiments are observed to be in excellent agreement with each other at essentially all E_0 and θ . Our experimental values follow the present MCOP SEPA and the SMCPP SEP of Barbosa et al [8] for $\theta \leq 20^{\circ}$ whereas their experimental DCSs are found to be significantly lower. At larger $\theta \ge 40^\circ$ both theories are higher than experiments which are all in excellent agreement. At the overlap, E_0 of 30 eV and 50 eV, the present experiments are also in excellent agreement except at small θ at 50 eV. At E_0 of 30 eV the DCSs of Barbosa *et al* [8] are higher than the present experimental DCSs. The good agreement between the CSUF and the UFSCar DCSs is encouraging, especially since (as described previously) both experiments use a different variation of the RFT and different setups. At large θ for $E_0 \ge 30 \text{ eV}$ the theories move higher up and further away from the experimental points. At 20 and 30 eV, the IAM SEPA results strongly disagrees with the experimental data as well as the MCOP SEPA and SMCPP SEP calculations, as expected since this is a poor model for describing low-energy e⁻-molecule scattering. However, a very good agreement is observed between IAM



Figure 6. (a) ICS and (b) MTCS for elastic electron scattering from chlorobenzene. Experiment: (●) CSUF data; (■) UFSCar data; (○) TCS of Makochekanwa et al [13]; theory: (- - -) SMCPP SEP calculation [8]; (---) MCOP SEPA calculation; (----) IAM-AR SEPA results.

SEPA and SMCPP at 50 eV for $\theta > 50^{\circ}$. At $E_0 = 100$ eV the IAM results show good qualitative agreement but stay higher than the experimental DCS values.

Figure 3 shows our measured DCSs in comparison with the IAM SEPA results for energies of 150 eV and above. The MCOP SEPA results are also shown for 150 eV. As can be seen, the calculated IAM-DCS demonstrates a qualitative agreement with experimental measurements, and the quantitative agreement is improved with increasing incident energies as expected. At the energies of 150 eV, a quite good agreement is observed between the experimental and the MCOP SEPA data for scattering angles below 50°. The oscillations observed in the MCOP calculations at higher angles are attributed to the lack of convergence in the partial-wave expansion of both the interaction potential and the T-matrix elements [58]. Unfortunately, there are no previous experimental or theoretical results to compare with the present results in this energy range.

In figure 4 we show experimental DCSs as a function of E_0 for $\theta = 90^\circ$ in a so-called 'excitation function'. We do not observe any resonant enhancement at $E_0 = 2.44$ eV feature observed by Skalický et al [12], and in fact this we see this E_0 value's excitation function $\theta = 90^\circ$ located at minimum. We are unfortunately unable to observe their $E_0 = 0.75$ eV

V A S da Mata et al

resonance feature as it is below our excitation energy curve. We observe a broad shape resonance at $E_0 \approx 8 \text{ eV}$ in agreement with the total cross section peak of Makochekanwa et al [13] at 8.5 eV. The fact that we cannot see the 2.44 eV resonance in the elastic channel in our experiment supports its connection with inelastic vibrational excitation of the C-Cl stretch vibration by temporary electron capture in the σ^*_{C-Cl} orbital as determined by Skalický et al [12].

In figures 5(a) and (b) we make a comparison of the available experimental DCSs for pertinent benzene derivatives. Table 1 has a summary of the molar masses and dipole moments for these benzene-related compounds. Here, o-xylene is selected for amongst the o- m- p-xylene compounds as it has the highest dipole moment of the three and highest representative cross sections. From the figures we observe that at E_0 of both 15 eV and 30 eV, o-xylene, benzonitrile DCSs are the largest at small θ which is due to a combination of having a large mass and dipole moment (see especially figure 5(b)). Trifluorotoluene, which has a large dipole moment (larger than toluene, see table 1), is below these two, but considering its large mass, its DCSs are much smaller at larger θ . As expected, benzene which has the smallest mass and no dipole moment has an overall lowest DCS of these compounds. All these molecules exhibit a characteristic angular behavior with forward scattering due to polarization effects (permanent dipole moment, or polarizability) followed by a shallow maximum in the θ range of between 50° to 110° and then some backward scattering due to short-range forces. With reference to these benzene derivatives, benzochloride DCSs are somewhat in the middle to lower middle of these DCSs.

4.2. Integral cross sections

In figures 6(a) and (b), we present our experimental ICS and MTCS, respectively, in the 1-800 eV range along with our MCOP and IAM-AR calculations. The ICS SMCPP results of Barbosa et al [8] and the experimental TCS of Makochekanwa et al [13] are shown for comparison. We see an excellent continuity between the CSUF and the UFSCar ICSs data sets as a function of E_0 . An excellent agreement with the TCSs is also observed. The TCSs rise above the ICSs as E_0 exceeds 15 eV i.e. when electronic inelastic and later ionization channels open up, as expected. The MCOP SEPA results show a good agreement with the SMCPP SEP data. However, both theoretical curves are in general above the experimental data with a better agreement between 2 and 10 eV for the SMCPP results. Besides, the broad feature centered at around 10 eV observed in both experimental ICS and TCS is well described by the MCOP calculation. The ICS IAM SEPA results strongly disagree with the experimental data in the entire angular range but it shows good qualitative behavior. In figure 6(b) a quite good agreement can be observed between the MTCS MCOP and the experimental results for energies below 10 eV. Above 20 eV, the MCOP SEPA is somewhat higher, but gets in reasonable agreement with the UFSCar data for E_0 of 100 eV and 200 eV. The two experimental data sets show a very clear dip in the MTCSs for E_0 values between 10 eV and 100 eV.

5. Conclusion

We have presented absolute DCS, ICS, and MTCS for the elastic electron collisions with chlorobenzene over a wide energy range (1–800 eV) E_0 values, extending the previous work of Barbosa *et al* [8] over both E_0 and θ . The present UFSCar and CSUF experimental results show mostly good agreement with [8] except at small θ at intermediate E_0 values of 20, 30, and 50 eV where differences are in some cases greater than factors of 2. Elsewhere (at larger θ) agreement between the present work and [8] is very good. The validity of our experimental data is vindicated by the good agreement between the measured DCSs of CSUF and UFSCar at overlapping energies of 20, 30, and 50 eV, although both laboratories used significantly different experimental setups and procedures. This, to some extent, resolves the possibilities of systematic differences in RFT measurements that use an aperture or a hypodermic needle collimator to produce the target gas beam. A comparison of the present results with other derivative benzene molecules as done showing the importance of the benzene group in the collision dynamics as far as dipole moments and mass sizes are concerned. We observe a good correlation of the increase in the size of the cross sections with the dipole moment for forwarding scattering DCSs, and (overall) with the mass for large θ scattering. Additionally, calculations using complex optical potentials were done using two different theoretical approaches, i.e. the MCOP SEPA in the 1 to 150 eV and standard IAM SEPA at 20 to 500 eV. The good overall agreement between our measured data and theoretical results as well as previous SMCPP theoretical results [8] over the complete E_0 range of the present work is encouraging. The results of the current investigation should be useful for modeling energy transfer processes with benzene-related compounds which are presently considered to be of environmental importance.

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