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Total cross section measurement for electron scattering from chlorine molecules in the energy region from 0.8 to 600 eV

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Abstract

Total scattering cross sections for chlorine molecules by electron impact are determined experimentally for impact energies from 0.8 to 600 eV. Elastic scattering cross sections are also determined theoretically. The results above 23 eV are the first rigorous report on these processes. The present results are compared, for the energy dependence and magnitude, with the previous measurements in the energy region they overlap. Well separated peaks are observed around 7.8 and 12 eV, with the one at 7.8 eV being attributed to dissociative electron attachment, while that at 12 eV is speculated to be due to ion-pair formation through direct dissociation. The present elastic cross sections are found to show a similar shape to the total cross section, although the magnitude is smaller by from a few per cent below 30 eV to a factor of two at 100 eV.

1. Introduction

Chlorine molecules are known to be one of the most effective gases for etching and widely used for semiconductor, thin-film manufacturing and other industrial applications [1]. By using electrons from a discharge, various inelastic processes, such as ionization, electronic excitation or dissociation of chlorine molecules are induced, and these ionized or excited species are often unstable and eventually dissociate. These fragmented chlorine atoms and ions are then introduced to surfaces for applications. Molecular chlorine is also of atmospheric and environmental interest [2]. For instance, it is a potential atmospheric reservoir of chlorine atoms [3], which are released photolytically,



Therefore, complete, comprehensive and systematic data for electron and ion impacts on chlorine molecules are undoubtedly needed. Unfortunately, however, studies on the scattering dynamics from this molecule have only rarely been carried out, because of the poisonous nature

of the gas, and, consequently, these scattering cross section data are not simply available for a variety of processes and a wide range of collision energies. Even total cross section (TCS) data in a wide energy range are not known, and above 23 eV absolutely no data for electron scattering exist to date. Therefore, we have undertaken this project to determine total scattering cross sections experimentally in a wide range of impact energies, and calculate elastic cross sections (ECSs) theoretically.

There have been three earlier attempts at experimental studies for TCSs at lower energies. In 1937, the first measurement was reported by Fisk [4] in the energy region from 2 to 40 eV, while more recent studies by Gulley *et al* [5] and Cooper *et al* [6] were concerned with the energy region from 23 down to 0.02 eV using transmission spectroscopy. The old results by Fisk [4] are larger by an order of magnitude than all other measurements discussed in this paper, and obviously these data had better be only considered as reference, and are thus not included for further discussions in this study. Theoretically, Rescigno [7] has recently calculated ECSs as well as dissociative excitation cross sections in the energy region from 0.2 to 30 eV. Based on the small numbers of investigations described above with additional spectroscopic experiments, Christophorou and Olthoff [8] tried to compile electron scattering data for chlorine molecules including total, elastic and various electronic excitation cross sections, although lack of sufficient information for any process hinders their effort from recommending the ‘best’ set of cross section data. They noted that, even in a case where fragmental data are available, wide discrepancies among them prohibit them from making an accurate determination of the cross section.

2. Experimental and theoretical procedures

2.1. Experimental method

2.1.1. Total cross section (TCS) measurements. The absolute TCSs for electron scattering from chlorine molecules have been measured for the energy range 0.8–600 eV using a linear transmission time-of-flight (TOF) method in an apparatus set-up similar to our previous measurements [9], as shown in figure 1. Some specific features of the experiment are summarized here. A $\sim 80 \mu\text{Ci}$ ^{22}Na radioactive source produces fast positrons, which are converted to a slow beam using an annealed tungsten ribbon moderator set. For electron scattering, the slow electrons are produced as secondary electrons emerging from the moderator surfaces after multiple scattering. The slow-electron beam had an energy spread of about 1.4 eV. The electrons that pass through the collision cell are transported into the detector by the magnetic field due to the solenoid. A retarding potential unit, inserted in front of the ceratron detector cone, is applied to eliminate contributions from large-energy-loss inelastic collisions and to decrease the effects of forward scattering due to elastically scattered electrons with reduced axial velocities resulting from angular deflection.

The TCS values, Q_t , are derived from the equation

$$Q_t = -\frac{1}{nl} \ln\left(\frac{I_g}{I_v}\right) \quad (1)$$

where I_g and I_v refer to the projectile beam intensities transmitted through the collision cell with and without the target gas of number density n , respectively. l refers to the effective length of the collision cell, and was established by normalizing our measured positron– N_2 TCSs to those of the positron– N_2 data of Hoffman *et al* [10]. Our present apparatus set-up has been specifically designed to have a collision cell with wide entrance and exit apertures for the weak positron beam intensities. The ceratron detector detects some projectiles scattered through small angles. In order to derive accurate TCSs for electron and positron scattering, it is

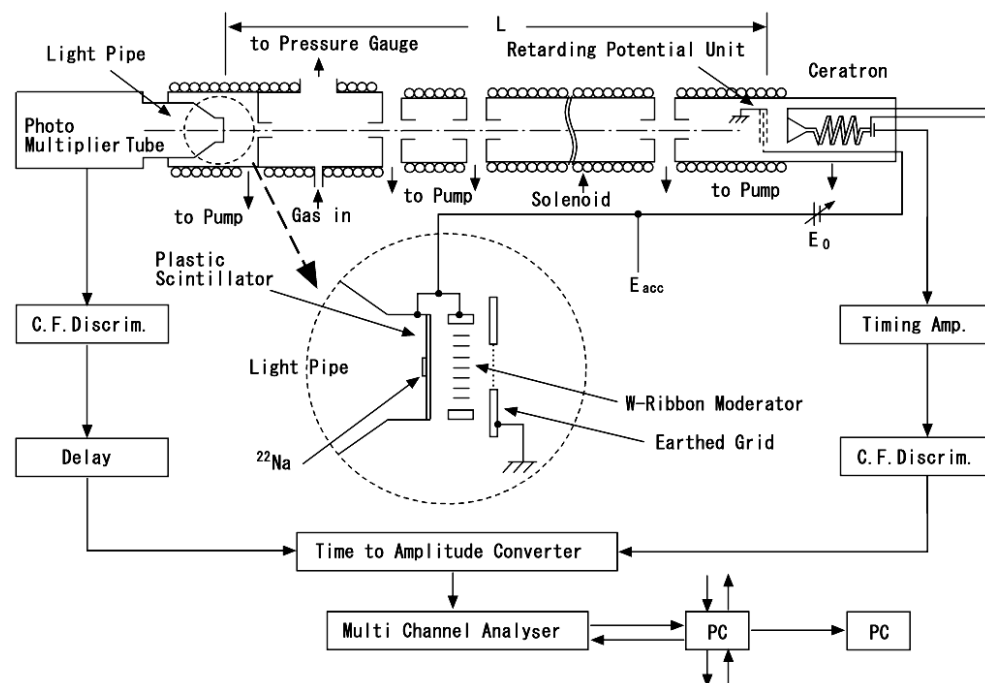


Figure 1. Schematic diagram of the apparatus and the main electronic circuits. The inset shows the arrangement of the ribbon moderator. The abbreviations are as follows: E_{acc} , acceleration potential; E_0 , a constant potential; $E_{acc} - E_0$, retarding potential; C. F. Discrim., constant fraction discriminator; PC personal computer.

necessary to account for this effect. For this, we take into account the collision cell geometry, the external magnetic field and the differential cross section (DCS) data from the experimental or theoretical results on the molecule being studied. The procedure for this has been described in detail previously [9]. The DCS data used for the correction for chlorine molecules are those of Gote and Ehrhardt [11]. For this paper, the correction for the electron TCSs amounts to 11–19% below 30 eV, but becomes smaller at higher energies, down to <6% for impact energies above 100 eV.

This gas presented a few problems, that included choking up some of our system's five rotary pumps. As a result, we had to reduce the measurement times usually necessary for better statistical errors for our electron TCSs. The experiments for TCS independence of gas pressure also had to be omitted. However, because all our other measurements with the same apparatus up to now have all proved the TCS independence of gas pressure [12], we infer the same here.

2.1.2. Errors in the measurements. The errors in the results are the total uncertainties. These total uncertainties were computed from the equation

$$\frac{\Delta Q_t}{Q_t} = \frac{\Delta n}{n} + \frac{\Delta l}{l} + \frac{\Delta I}{I}. \quad (2)$$

This sum of all the uncertainties was estimated to be 4.5–6%. These uncertainties are made up of contributions from the <2% electron beam intensities, $\Delta I/I$, where I refers to $\ln(I_g/I_v)$ in equation (1), the contribution from the gas density, $\Delta n/n$, which was <2% for this target

molecule in gas form, and that due to the determination of the effective length of the collision cell, $\Delta l/l$, which was about 3%. Because of the troubles highlighted in section 2.1.1 above, the error rates in the present data are relatively high compared to our other measurements.

2.2. Theoretical model

The theoretical approach employed is the continuum multiple-scattering (CMS) method, which is a simple but efficient model for treating electron scattering from polyatomic molecules [13]. In order to overcome difficulties arising from

- (i) the many degrees of freedom of electronic and nuclear motions and
- (ii) the non-spherical molecular field in polyatomic molecules,

the CMS uses the technique to divide the configuration space into three regions: the atomic region surrounding each atomic sphere, the interstitial region and the outer region surrounding the molecule. The scattering part of the method is based on the static-exchange-polarization potential model within the fixed-nucleus approximation. The Schrödinger equation in each region is solved numerically under separate boundary conditions, and by matching the wavefunctions and their derivatives from each region we can determine the total wavefunctions of the scattered electron and, hence, the scattering matrix. The scattering cross section can be easily determined by a conventional procedure.

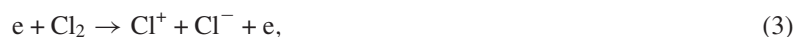
3. Results and discussion

3.1. TCSs

Figure 2 shows the present TCSs for the entire energy range measured, together with the previous three sets of experimental results for lower energies. The present results are found to be in reasonable accord with those of Gulley *et al* [5] and Cooper *et al* [6] in the energy dependence, although the present results are smaller by about 30% compared to those of Gulley *et al* [5] over the whole energy where we overlap, and are smaller than those of Cooper *et al* [6] by an average of 18% below 8 eV, with the difference narrowing above 8 eV to within 10%.

There are a number of interesting features generally revealed by all these results, as shown in figure 2, and these are summarized as follows.

- (i) All TCSs increase with increasing impact energies from 0.8 eV to peak at about 10 eV before showing a gradual decrease with increasing energy above 15 eV.
- (ii) A weak unresolved structure is seen at 2.5 eV. This resonant feature arises from the 2.5 eV $^2\Pi_g$ state causing the dissociative electron attachment (DEA), which was studied experimentally by Kurepa and Belic [14] and also seen in the data of Tam and Wong [15].
- (iii) A relatively strong peak is seen near 7 eV. This peak is known to correspond to the formation of the negative-ion state through a $^2\Pi_u$ resonance in the DEA [14, 15], overlapping with the lowest Feshbach resonance of Cl_2 , which has been identified by Spence [16] in an electron transmission experiment.
- (iv) An unpronounced minimum is observed at about 11.5 eV in the present result as well as that of Cooper *et al* [6]. This feature appears to indicate the presence of some weak process in the DEA cross section data of Kurepa and Belic [14].
- (v) A relatively weak peak is seen in the energy region between 12 and 14 eV. This peak, however, unlike the others highlighted above, may not be solely due to the DEA channel but rather also due to contributions from



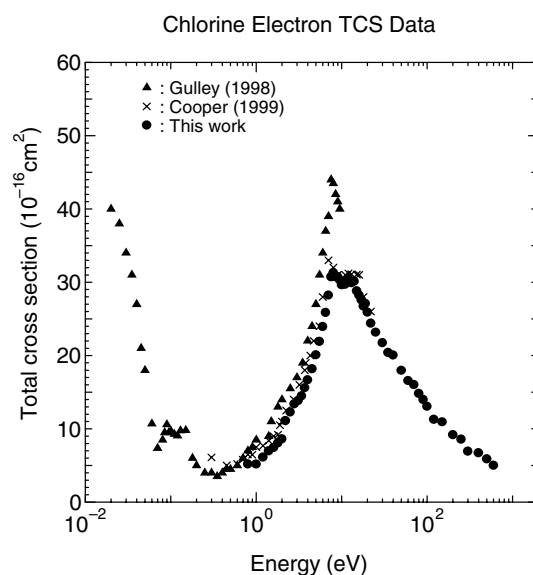


Figure 2. TCS of chlorine molecules by electron impact. ●, the present result; ▲, Gulley *et al* [5]; ×, Cooper *et al* [6].

i.e. ion-pair formation, which is seen as having a threshold energy of 11.9 eV in the result of Kurepa and Belic [8, 14], and possibly the contributions from indirect electron attachment processes as well.

- (vi) The weak change of the slope, or shoulder, in the region 69–80 eV is observed in our TCSs. More marked structure was found in the ionization cross section (ICS) of Stevie and Vasile [17], which could also be due to contributions from the ion-pair formation process that, as studied by Kurepa and Belic [14], exhibits a peak between 70 and 90 eV.

A few comments on our smaller TCSs compared to other measurements may be appropriate here. The measurements of Gote and Ehrhardt [11] on rotational scattering from Cl_2 , as well as observations by Cooper *et al* [6], showed that forward scattering is very appreciable over all energies and at angle $\leq 2^\circ$. Thus, though we took the forward scattering corrections into account for evaluation of TCSs, they may not have been sufficient, resulting in the underestimation of our values.

3.1.1. Comparison of TCS, elastic and ionization cross sections. In figure 3, our measured TCSs and our calculated ECSs as well as ICSs by Kurepa and Belic [14] are all displayed. Our ECSs are found to be only slightly smaller in magnitude than TCSs below 7 eV, while the difference increases as the energy increases. The ECS becomes smaller by about a factor of two than the TCS at 100 eV. The present ECSs are found to agree reasonably well with the other theoretical results of Rescigno [7]. Nearly identical values of TCSs and ECSs may be attributable to a combination of slight underestimation of TCSs as discussed above and slight overestimation of ECSs. Below 10 eV or so, TCSs would be constituted primarily of elastic, electronic excitation and ro-vibrational excitation channels. According to the estimate by Christophorou and Olthoff [8], electronic excitation and ro-vibrational excitation cross sections are small with values of around 10^{-16} cm^2 (except for the resonance region at 11 eV), whereas the present TCSs and ECSs are much larger with values in the neighbourhood of a few

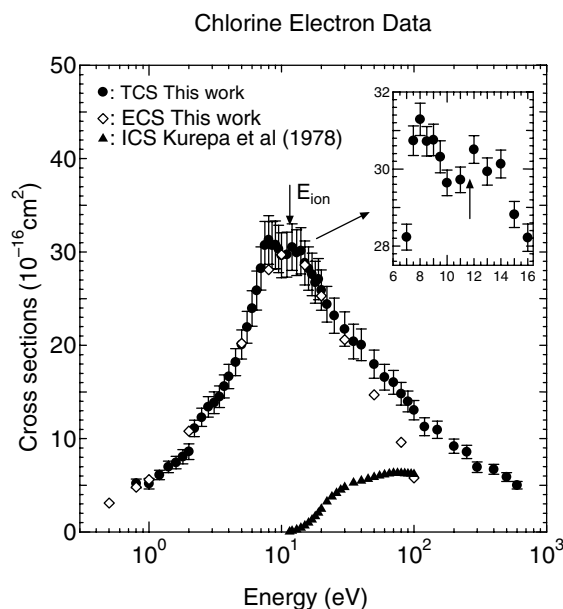


Figure 3. TCSs, ECSs and ICSs of chlorine molecules by electron impact. ●, present TCSs; ◇, present ECSs; ▲, ICSs by Kurepa and Belic [14]. The vertical arrow indicates the threshold energy of ionization. Error bars indicate the total uncertainties. Inset: the vertical arrow indicates the threshold for ion-pair formation [7, 13].

times 10^{-15} cm^2 . Hence, the contribution from these excitations to TCSs could be not more than a few per cent below a few electronvolts energy. Consequently, these relatively close values of TCSs and ECSs may not be so unreasonable. Nevertheless, it would be desirable to examine this overestimation of theoretical ECSs more carefully.

ICSs begin to grow rapidly soon after the threshold of 11 eV, and reach the maximum with a value of $6.5 \times 10^{-16} \text{ cm}^2$ at 100 eV which amounts to more than 50% of the TCS. The difference between TCS and a sum of ECS and ICS accounts for electronic excitation including ion-pair formation and ro-vibrational excitation cross sections. At lower energies, ro-vibrational excitations dominate, while electronic excitations take over at higher energies, causing the different energy dependence for the contribution.

3.1.2. Comparison between the chlorine TCSs and the ethane TCSs. Systematic inspection of various TCSs for various molecules led us to draw figure 4, which shows a comparison between our experimental chlorine (Cl_2) and ethane (C_2H_6) TCSs. At first glance, it would be quite strange to compare these two completely different molecules, since the relation between the two appears to be remote. However, as described below, there are some interesting similarities between the two, which may warrant some attention for careful examination.

The general shape and magnitude of these two TCS results is found to be surprisingly similar. The ethane TCSs are larger by 20% than the chlorine TCSs below 10 eV, while the TCSs for these two molecules are very close to each other, less than 10%, above 10 eV. Though the spike in the chlorine TCSs at 2.5 eV is not reflected in the ethane, the rather strong peak at 7.5 eV is also seen in the ethane TCSs. The TCSs for these two molecules become almost equal in size above 30 eV, a feature attributable to the similarity in molecular size (see below).

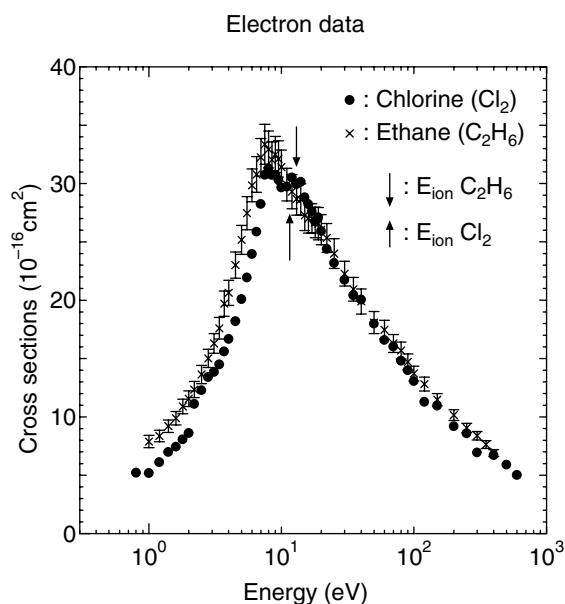


Figure 4. TCSs for chlorine molecules (Cl_2) and ethane (C_2H_6). ●, chlorine; ×, ethane. Error bars indicate statistical errors.

Table 1. Molecular properties of the chlorine molecule and ethane [17].

	Chlorine (Cl_2)	Ethane (C_2H_6)
Electronic configurations:	$\dots (\sigma_g 3p)^2 (\pi_u 3p)^4 (\pi_g 3p)^4 (\sigma_u 3p)^0$	$\dots (2a_1)(2a_{2u})^2 (1e_u)^4 (3a_{1g})^2 (1e_g)^4$
Number of valence electrons:	14	14
Ionization potentials (eV):	11.48	11.49
Bond length and angles:	Cl–Cl, 1.9878 Å	C–C, 1.5351 Å C–H, 1.0940 Å $\angle\text{CCH}$, 111.17°
Polarizability (au):	4.61	4.47

As compared in table 1, various molecular properties of the two molecules, such as the size (a Cl–Cl length of 1.99 Å for Cl_2 versus 2.33 Å for the $\text{CH}_3\text{--CH}_3$ length in C_2H_6), the number of valence electrons (14 electrons for both), ionization potentials (nearly identical for both) and polarizability (4.61 au for Cl_2 versus 4.47 au C_2H_6), are very close, or comparable, to each other. Particularly, the close values of the polarizability are believed to be responsible for this similarity in TCSs in the higher energy region, while the similar size, and the same number of valence electrons, may in some part reflect the similarity in size and shape of TCSs on the lower energy side. Certainly, it may be just a coincidence, but further detailed theoretical and experimental investigations on this strikingly similar shapes and magnitudes of the two TCSs are warranted.

4. Conclusions

Since chlorine molecules are one of the most important gases for etching of various thin metal films and hence electron scattering cross section data are required for applications, we have

carried out experimental investigations for electron scattering from chlorine molecules for understanding scattering dynamics and determining TCSs accurately, which cover the energy range from 0.8 to 600 eV. ECSs are also determined theoretically. As for our TCSs, their general shape and magnitude are found to agree reasonably well with those of Cooper *et al* [6] below 10 eV. They are, however, about 30% smaller than those of Gulley *et al* [5] over the whole range of overlap. They have two strong peaks due to shape resonances at 7.8 and 12 eV, which are associated with dissociative attachment and ion-pair formations, respectively, followed by a sharp decrease beyond this energy. ECSs are found to be smaller by only a few per cent than present TCSs, and we consider this as being likely to be from the overestimation of ECSs in the present theory although the general shape is in good harmony with the TCSs. These cross sections should be of good use for applications.

Acknowledgments

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