Experimental absolute electron impact ionization cross-sections of Cl\(_2\)

R Basner\(^1\) and K Becker\(^2\)

\(^1\) Institut für Niedertemperatur-Plasmaphysik, Friedrich-Ludwig-Jahn-Strasse 19, D-17489 Greifswald, Germany
\(^2\) Department of Physics and Engineering Physics and Center for Environmental Systems, Stevens Institute of Technology, Hoboken, NJ 07030, USA
E-mail: basner@inp-greifswald.de and kbecker@stevens.edu

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Abstract. We measured absolute partial cross-sections for the formation of Cl\(_2^+\), Cl\(_2^{2+}\), Cl\(^+\) and Cl\(^{2+}\) ions following electron impact on molecular chlorine (Cl\(_2\)) from threshold to 900 eV using a time-of-flight mass spectrometer. The ion spectrum at all impact energies is dominated by the singly charged ions with maximum cross-section values of 4.6 \(\times\) 10\(^{-16}\) cm\(^2\) for Cl\(_2^+\) at 32 eV and 4.0 \(\times\) 10\(^{-16}\) cm\(^2\) for Cl\(^+\) at 70 eV. The cross-sections for the formation of the doubly charged ions are more than one order of magnitude lower. Double ionization processes account for about 6% of the total ion yield at 70 eV. The absolute total ionization cross-section of Cl\(_2\) was obtained as the sum of all measured partial ionization cross-sections. To the extent possible, a comparison of our results with other available measured and calculated data is made.

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1. Introduction

In an effort to understand the electron ionization processes and develop models of the chemistry occurring in technologically important low-temperature plasmas, various reliable cross-sections for the electron impact ionization and dissociative ionization are needed. Recent work on the interactions of molecular chlorine (Cl\textsubscript{2}) with electrons is largely motivated by the importance of this molecule for plasma-etching applications. Cl\textsubscript{2} is widely used as the main constituent or an admixture in processing plasmas feed gas mixtures that are used to etch silicon [1]–[4], different other semiconductor materials [5]–[8] and various metals and metal oxides [9]–[12].

Recently, Christophorou and Olthoff [13] published a comprehensive review of critically evaluated and assessed data for fundamental interactions of low-energy electrons with Cl\textsubscript{2} by updating and expanding previous data compilations [14]. Although the electron impact and ion transport database of Cl\textsubscript{2} is more extensive compared with similar databases for other plasma processing gases, it is not complete and a significant number of the available data have not been confirmed by more than one independent measurement or by a stringent comparison between measurement and calculation [13]. Total electron impact ionization cross-sections of Cl\textsubscript{2} were measured by Center and Mandl [15], Kurepa and Belic [16], Stevie and Vasile [17] and Srivastava and Boivin in [13]. The four data sets differ in the magnitude of the reported cross-sections as well as in the measured energy dependence. The cross-section values vary from $0.25 \times 10^{-16}$ to $5.1 \times 10^{-16}$ cm\textsuperscript{2} at 20 eV impact energy and from $5.5 \times 10^{-16}$ to $7.1 \times 10^{-16}$ cm\textsuperscript{2} at 70 eV [13]. The results of recent calculations of the total Cl\textsubscript{2} ionization cross-section were also summarized in the review of Christophorou and Olthoff [13]. These calculations show noticeable differences between each other, but are in reasonable agreement (within the margin of experimental uncertainty) with the measurements of Stevie and Vasile [17]. The database on partial ionization cross-sections for Cl\textsubscript{2} is rather limited. Calandra et al [18] measured relative partial cross-sections for the formation of Cl\textsubscript{2}+, Cl\textsuperscript{+} and Cl\textsuperscript{2+} in the energy range from 25 to 200 eV using a time-of-flight mass spectrometer (TOF-MS). Recently, Pal et al [19] have calculated absolute partial cross-sections for the formation of Cl\textsubscript{2}+, Cl\textsuperscript{2+} and Cl\textsuperscript{+} based on the measured and normalized photo-ionization cross-sections of Samson and Angel [20]. However, the measured branching ratio Cl\textsuperscript{+}/Cl\textsubscript{2+} [18] is much larger (about four times at an impact energy of 35 eV) than the ratio of the calculated cross-sections [19]. Also, the measured and calculated energy dependences are completely different, even if the contributions of Cl\textsuperscript{+} ions from multiple ionization are removed from the measured data. Obviously, the availability of reliable absolute ionization data for Cl\textsubscript{2} is unsatisfactory.

Here, we report measured electron-impact ionization cross-section data for Cl\textsubscript{2} in the energy range from threshold to 900 eV obtained in a TOF-MS that allows us to determine reliable absolute partial ionization cross-sections without mass discrimination of the energetic fragment ions.

2. Experimental details

The measurements were carried out using a TOF-MS shown schematically in figure 1. The instrument and the data acquisition and analysis procedures have been described in detail before [21]–[23] and the reliability of this mass spectrometric technique for the measurement for absolute partial ionization cross-sections of energetic fragment ions was demonstrated for the plasma processing gases TiCl\textsubscript{4}, SiF\textsubscript{4}, CF\textsubscript{4}/C\textsubscript{2}F\textsubscript{6}, B\textsubscript{2}H\textsubscript{6} and WF\textsubscript{6} [21]–[25]. Briefly, the TOF-MS
can be operated either in a linear mode using detector I or in a reflection mode using the reflector (grids: G3–G5) and detector II. In the present study, all measurements for the determination of the partial ionization cross-sections were performed with the TOF-MS operated in the linear mode to ensure complete transport of energetic fragment ions from the ion source to the detector and to reduce the data collection time by operating the instrument at a maximum repetition frequency of 20 kHz. Additionally, the reflection mode was used successfully to confirm the results at fixed impact energy of 70 eV. The ion source chamber was filled with a well-defined Cl₂/Ar mixture through precision leak valves up to partial pressures of about 1 × 10⁻⁴ Pa in an effort to facilitate the simultaneous measurements of the ions from Cl₂ and Ar under identical operating conditions. The relative partial Cl₂ ionization cross-sections were put on an absolute scale by normalization relative to the partial Ar⁺ ionization cross-section of 2.52 × 10⁻¹⁶ cm² at 70 eV [26]. Taking into account the uncertainties of ±5% in the Ar reference cross-section [26], the statistical uncertainty in our pressure measurement of ±3% and an uncertainty of typically ±3–7% resulting from the counting statistics, we assign an overall uncertainty of ±15% to the absolute ionization cross-sections reported here.

Typically, the electron gun was operated using electron pulses of 100 ns width. The electron beam has a diameter of about 0.6 mm in the interaction region and the amplitude of the electron pulse was in the range from 1 to 10 µA with an energy spread of about 0.5 eV (FWHM). The impact energy was varied from 5 to 900 eV and the electron beam was guided by a weak magnetic field (200 G). A voltage of 1 kV (extraction fields of 1 kV cm⁻¹) was applied to the repeller, roughly 10 ns after the incident electron pulse passed through the ionization region.
This extraction pulse accelerates the ions formed by electron impact towards the grounded ion source exit aperture and the entrance electrode of the flight tube, which is held at a $-2.8 \text{ kV}$ bias voltage. We maintained operating conditions under which 100% ion transmission of all ions from the ion source to the detector was established with the exception of ion losses at the grids $G_1$ and $G_2$. The output signal from the respective MCP passes a preamplifier, a constant fraction discriminator and is recorded with a 2 GHz multiscaler (Model 7886; FAST ComTec) with a time resolution of 500 ps. Our TOF-MS was operated in such a way that no more than one ion of the most intense ion signal was created during each electron pulse. This resulted in low overall count rates and comparatively long data acquisition times, but ensured, on the other hand, that dead time corrections to the recorded signal rates were negligible.

3. Results and discussions

The mass spectra of positive ions resulting from electron impact on Cl$_2$ at 70 eV impact energy derived from measurements carried out with the TOF-MS operated in the linear mode and in the reflection mode confirm the expected isotopic distributions due to the natural isotopic abundances of 75.8% for $^{35}\text{Cl}$ and 24.2% for $^{37}\text{Cl}$ [27]. We observe a relative intensity of Cl$^+$ that is 10% higher compared with the mass spectrum found in the NIST database [28]. The reason for this discrepancy may be the optimized detection efficiency of our TOF-MS for energetic fragment ions. This optimization is usually not done for quadrupole mass spectrometers that are most commonly used in analytical mass spectrometry. We carried out qualitative checks of the excess kinetic energy for fragment ions Cl$^+$ and Cl$^{2+}$ by performing a full horizontal sweep of the extracted ion beam using a double-focusing mass spectrometer and comparing the shapes with the Cl$_2^+$ and Cl$_2^{2+}$ ion signals, which are characteristic of a beam of ions without excess kinetic energy and show identical shapes as Ar$^+$ and Ar$^{2+}$ [21, 24]. The curves of the two fragment ions (see figure 2) show a distinct broadening which is indicative of a broad distribution of excess...
kinetic energies. The Cl₂ mass spectrum in the NIST database [28] does not show any doubly charged ion signal at all. We identified the Cl²⁺ ion at mass numbers 17.5 and 18.5 and in addition the ³⁵Cl³⁷Cl²⁺ ion at mass number 36. Using the known isotopic abundances, we calculated the respective ³⁵Cl²⁺ and ³⁷Cl²⁺ ion currents and corrected the ³⁵Cl⁺ and ³⁷Cl⁺ ion signals at the same mass numbers for all impact energies. The partial ionization cross-sections were then obtained by adding the individual isotope contributions. The thresholds of the particular ionization curves with their respective uncertainties confirm the known values of the appearance energies for Cl₂⁺, Cl₂²⁺, Cl⁺ [13, 29] and Cl²⁺ [18].

The numerical values of the partial ionization cross-sections for the formation of singly charged ions, the partial counting ionization cross-sections for the formation of doubly charged ions, and the total ionization cross-section (the charge-weighted sum of all partial cross-sections) as a function of the energy of the ionizing electrons from threshold to 900 eV are given in table 1. The corresponding cross-section curves of the singly and doubly charged ions are shown in figure 3(a) (singly charged ions) and figure 3(b) (doubly charged ions) from threshold to 200 eV. It is obvious from the cross-section curves shown in figures 3(a) and (b) that direct ionization of Cl₂ to form Cl₂⁺ is the dominant process in the entire range of impact energies, although above 40 eV almost as many Cl⁺ ions are formed as Cl₂⁺ ions. The cross-sections of Cl₂⁺ increase rapidly from threshold to a narrow maximum of $4.59 \times 10^{-16}$ cm² at 32 eV and then decrease to a minimum at 46 eV and increase again to a broad maximum of $4.55 \times 10^{-16}$ cm² at 80 eV followed by a gradual decrease towards higher impact energy. This energy dependence of the cross-sections, which was also found for the electron impact ionization of TiCl₄ [21], may be a result of an auto-ionization channel competing with direct ionization [30]. This indirect ionization process is expected to be more prominent in the low-energy range and is a resonance process. The cross-section curves of the other three ions all show the more conventional cross-section shape, which shows an increase from threshold to a maximum around 70–100 eV followed by a gradual decrease towards higher impact energies. Figure 3(a) also shows the calculated partial cross-sections of Pal et al [19] for Cl₂⁺ and Cl⁺. Their results differ from our data for Cl₂⁺ in the energy dependence and in the absolute values and for Cl⁺ in the absolute values by a factor of 4.

The ion spectrum in the lower energy region, which is of special interest for low-temperature plasma technology, is dominated by Cl₂⁺. For example, Cl₂⁺ accounts for 95% of the total ionization cross-section value at 15 eV and for 88% at 20 eV.

Doubly charged ions appear at energies above 32 eV in case of Cl₂²⁺ and above 40 eV for Cl²⁺. These cross-sections reach their maximum values at energies of 80 and 100 eV, respectively (see table 1 and figure 3(b)). The maximum cross-section values are more than one order of magnitude lower compared with those of the singly charged ions. The charge-weighted sum of the doubly charged fragment ions accounts for about 7.6% of the total ionization cross-section of Cl₂ at 100 eV. Figure 3(b) also shows the calculated partial cross-sections of Pal et al [19] for Cl₂²⁺. Their result for Cl₂²⁺ differs from ours in the energy dependence and in the absolute value by a factor of 24.

It is possible to compare the energy dependence of the partial cross-sections measured as part of this work with the relative partial cross-sections reported recently by Calandra et al [18] in the energy range from 25 to 200 eV. Since their measurements were not absolute, we can only compare the ratio of partial cross-sections. Figure 4 shows the ratios of the partial cross-sections $Q_r(Cl⁺/Cl₂⁺)$ and $Q_r(Cl²⁺/Cl₂⁺)$ from our data in comparison with the data of [18]. Since Calandra et al [18] did not report separate cross-section curves for the formation of Cl⁺ and Cl₂⁺,
Table 1. Absolute partial counting and total (charge-weighted) electron impact ionization cross-sections for Cl₂ as a function of electron energy.

| Electron energy (eV) | Cl₂⁺ | Cl⁺ | Cl₂⁺⁺ | Cl³⁺ | Total |
|----------------------|------|-----|-------|------|-------|
| 12                   | 0.100| 0.100|       |      | 0.100 |
| 13                   | 0.346| 0.014|       |      | 0.360 |
| 14                   | 0.746| 0.032|       |      | 0.778 |
| 15                   | 1.13 | 0.055|       |      | 1.19  |
| 16                   | 1.58 | 0.081|       |      | 1.66  |
| 17                   | 2.00 | 0.126|       |      | 2.13  |
| 18                   | 2.39 | 0.209|       |      | 2.60  |
| 19                   | 2.72 | 0.297|       |      | 3.02  |
| 20                   | 3.13 | 0.435|       |      | 3.57  |
| 22                   | 3.65 | 0.715|       |      | 4.37  |
| 24                   | 4.00 | 1.08 |       |      | 5.08  |
| 26                   | 4.30 | 1.43 |       |      | 5.73  |
| 28                   | 4.49 | 1.85 |       |      | 6.34  |
| 30                   | 4.57 | 2.18 |       |      | 6.75  |
| 32                   | 4.59 | 2.67 |       |      | 7.26  |
| 34                   | 4.54 | 2.93 |       |      | 7.47  |
| 36                   | 4.44 | 3.13 | 0.003 |      | 7.58  |
| 38                   | 4.36 | 3.30 | 0.010 |      | 7.68  |
| 40                   | 4.31 | 3.40 | 0.021 |      | 7.75  |
| 42                   | 4.28 | 3.55 | 0.030 |      | 7.89  |
| 44                   | 4.26 | 3.63 | 0.048 | 0.005| 7.99  |
| 46                   | 4.25 | 3.68 | 0.070 | 0.013| 8.10  |
| 48                   | 4.27 | 3.74 | 0.089 | 0.033| 8.26  |
| 50                   | 4.31 | 3.80 | 0.099 | 0.045| 8.40  |
| 52.5                 | 4.34 | 3.85 | 0.104 | 0.078| 8.56  |
| 55                   | 4.38 | 3.87 | 0.109 | 0.099| 8.67  |
| 57.5                 | 4.41 | 3.90 | 0.112 | 0.112| 8.76  |
| 60                   | 4.43 | 3.95 | 0.117 | 0.121| 8.86  |
| 65                   | 4.49 | 3.99 | 0.123 | 0.139| 9.00  |
| 70                   | 4.52 | 4.03 | 0.127 | 0.152| 9.11  |
| 80                   | 4.55 | 4.01 | 0.129 | 0.190| 9.20  |
| 90                   | 4.51 | 3.9  | 0.128 | 0.207| 9.08  |
| 100                  | 4.50 | 3.84 | 0.123 | 0.221| 9.03  |
| 120                  | 4.41 | 3.67 | 0.106 | 0.216| 8.73  |
| 140                  | 4.17 | 3.35 | 0.096 | 0.205| 8.12  |
| 160                  | 4.12 | 3.23 | 0.084 | 0.187| 7.89  |
| 180                  | 4.03 | 3.04 | 0.075 | 0.171| 7.56  |
| 200                  | 3.87 | 2.86 | 0.068 | 0.158| 7.18  |
| 300                  | 3.22 | 2.16 | 0.054 | 0.122| 5.73  |
| 400                  | 2.79 | 1.76 | 0.043 | 0.102| 4.84  |
| 500                  | 2.45 | 1.45 | 0.029 | 0.091| 4.14  |
| 600                  | 2.14 | 1.25 | 0.020 | 0.078| 3.59  |
| 700                  | 1.98 | 1.11 | 0.016 | 0.071| 3.26  |
| 800                  | 1.80 | 0.973| 0.012 | 0.063| 2.92  |
| 900                  | 1.63 | 0.890| 0.011 | 0.062| 2.67  |
Figure 3. (a) Present absolute partial Cl$_2$ ionization cross-sections of Cl$_2^+$ and Cl$^+$ along with calculated data from [19] as a function of electron energy up to 200 eV. (b) Present absolute partial Cl$_2$ ionization cross-sections of Cl$_{2}^{2+}$ and Cl$^{2+}$ along with calculated data from [19] as a function of electron energy up to 200 eV.

we also included the cross-section ratio $Q_r((\text{Cl}^++\text{Cl}_2^{2+})/\text{Cl}_2^+)$ based on our data. Within the margin of error there is good agreement between the cross-section ratios derived from our data and the data of [18].

The present total Cl$_2$ ionization cross-section is shown in figure 5 up to 200 eV along with the present total single Cl$_2$ ionization cross-section and some previously reported experimental and theoretical results. The total ionization cross-section curve of molecular chlorine (last column of table 1) is derived as the charge-weighted sum of the four partial ionization cross-sections reported here. The total ionization cross-section exhibits a maximum at 80 eV with a peak value

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**Figure 4.** Present cross-section ratios $Q_r(Cl^+/Cl_2^+)$, $Q_r((Cl^+ + Cl_2^{2+})/Cl_2^+)$, and $Q_r(Cl_2^+ / Cl_2^+ \times 10$ along with measured data from [18] as a function of electron energy up to 200 eV.

**Figure 5.** Present absolute total Cl$_2$ ionization cross-sections and absolute total single Cl$_2$ ionization cross-sections along with previously reported experimental (exp.) and theoretical (calc.) results as a function of electron energy up to 200 eV.

of $9.2 \times 10^{-16}$ cm$^2$. Also shown in figure 5 are the total cross-sections from Kurepa and Belic [16], Stevie and Vasile [17], and an unpublished calculation taken from [13]. Additionally shown in figure 5 are unpublished calculations for the total single ionization cross-section also taken from [13]. Clearly, our results exceed all the other data with increasing impact energy including...
the suggested total cross-section of Christophorou and Olthoff [13], which is an average of data from [16, 17]. We note that several independent measurements with the TOF-MS in the reflection mode confirmed the absolute cross-section values reported here at the fixed impact energy of 70 eV.

4. Conclusions

We measured for the first time the absolute partial electron ionization cross-sections for the Cl₂ molecule using a time-of-flight mass spectrometric technique. A complete set of the absolute ionization cross-sections for the formation of Cl₂⁺, Cl₂²⁺, Cl⁺ and Cl²⁺ from Cl₂ was determined in the energy range from threshold to 900 eV. Direct ionization of Cl₂ to form Cl₂⁺ was found to be the dominant process in the entire range of impact energies and shows a pronounced maximum around 30 eV. The energy dependence and the relative partial ionization cross-section are in excellent agreement with recently measured relative cross-sections [18], but show significant discrepancies in comparison with theoretical predictions [19]. The derived absolute total ionization cross-section values are generally higher than all previous experimental and calculated data sets. The absolute cross-section values measured here are an essential contribution to complete the database on electron interactions with molecular chlorine, which is indispensable for a microscopic understanding and the detailed modelling of Cl₂-containing plasmas. The data presented here are also important for the critical evaluation of quantitative mass spectrometric plasma diagnostics data.

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