A critical review of the reaction set for a low pressure chlorine processing discharge

E. G. Thorsteinsson, A.Th. Hjartarson and
J. T. Gudmundsson

RH-16-2008

Jón Tómas Guðmundsson
tumi@raunvis.hi.is
Science Institute, University of Iceland
Dunhagi 3, IS-107 Reykjavik

December 2008

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Eyþór Gísli Þorsteinsson,
Aron Þór Hjartarson
&
Jón Tómas Gudmundsson

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Science Institute
University of Iceland

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E. G. Thorsteinsson, A. Th. Hjartarson and J. T. Gudmundsson

Department of Electrical and Computer Engineering,
University of Iceland,
Hjardarhaga 2-6, IS-107 Reykjavík, Iceland
and
Science Institute, University of Icealand,
Dunhaga 3, IS-107 Reykjavík, Iceland

December 28, 2008

Abstract

The rate coefficients for a low pressure chlorine processing discharge are evaluated and revised. We assume the electron energy distribution to be Maxwellian-like and the fit to the rate coefficient is valid in the range $1 - 7$ V.

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1   Introduction

Chlorine plasmas play a crucial role in integrated circuit fabrication. Chlorine gas is widely used in the plasma etching of semiconductors, in particular silicon. In such applications the chlorine molecules are dissociated in the discharge and the chlorine atoms etch the silicon substrate. There have been several attempts to assemble a reaction set and to model the chlorine discharge (Rogoff et al., 1986; Meeks and Shon, 1995; Lee and Lieberman, 1995; Lee et al., 1996, 1997; Malyshev and Donnelly, 2000; Hsu et al., 2006; Efremov et al., 2007). The electron impact cross sections for the chlorine molecule have been reviewed by Christophorou and Olthoff (1999) and Morgan (1992). In the current study we will consider the ground state chlorine molecule $Cl_2(X\,^1\Sigma_g^+, v = 0)$, the vibrationally excited ground state chlorine molecules $Cl_2(X\,^1\Sigma_g^+, v = 1 - 3)$, the ground state chlorine atom $Cl(3p^5\,^2P)$, the negative chlorine ion Cl^- and the positive chlorine ions Cl^+ and Cl_2^+.

Throughout the text we use the roman typeface symbol T for the voltage equivalent of the temperature. The aim of this work is to evaluate and revise the rate coefficients in a chlorine processing discharge, $T_e \approx 1 - 7$ V and $T_i \ll T_e$, where T_e is the electron temperature and T_i is the ion temperature. The rate coefficients for electron impact collisions were calculated assuming Maxwellian electron energy distribution and fit over an electron temperature range $1 - 7$ V.

2   The discharge species

The most basic species in the chlorine discharge are the neutral chlorine molecule in the ground state, the neutral chlorine atom in the ground state, the negative atomic ion Cl^- and the positive ions Cl_2^+ and Cl^+. Here we will discuss the other species that are likely to have an effect on the chlorine discharge but are generally not considered by modelling studies.

2.1 The Cl_2^- anion

Although it has been acknowledged that the Cl_2^- anion might have an impact on the chemistry of chlorine discharges (Christophorou and Olthoff, 1999), we are not aware of any modelling studies that have considered this negative ion as a part of the reaction set. Therefore, we have evaluated the possibility of including the anion in the current study.

According to the potential energy curves for Cl_2^- (Christophorou and Olthoff, 1999), only the ground state of the anion is stable and does not dissociate automatically. Thus, the molecular negative ion Cl_2^- cannot simply be formed in an electron attachment of Cl_2 because it must end up in an excited state in order for momentum to be conserved. This excited Cl_2^- is in all cases unstable and will dissociate quickly if not stabilized by a collision of a third particle. Three-particle reactions are not likely to be important at the low pressure of interest in the current study and because of the absence of any information of a third order electron attachment rate coefficient forming a stable Cl_2^- anion, we will not consider the process for the time being. In the case of the electronegative oxygen discharge, the negative ion O_2^- is mainly formed by dissociative attachment of O_3 (Gudmundsson et al., 2001). Thus, in order to properly include the Cl_2^- negative ion, the Cl_3 neutral and perhaps also the Cl_3^- anion would need to be included in the reaction set. Unfortunately, reactions leading to creation and destruction of polyatomic chlorine molecules or anions are far less documented than for e.g. oxygen and it seems that too little data is available to reproduce the Cl_3 or Cl_3^- density reliably. Therefore, we will not consider the Cl_3 or Cl_3^- particles and, as a consequence, the Cl_2^- anion in the current study.

2.2 Metastable species

Most electronic excitations of the chlorine molecule are dissociative and therefore excited chlorine molecules are not expected to have a large density in the discharge. Wise et al. (1995) examined the effects of metastable atomic states in chlorine and concluded that metastable atomic states have insignificant effect on the gas composition in chlorine discharges. Lee and Lieberman (1995) reached the same conclusion by pointing out the amount of energy needed

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to excite the chlorine atom and relating it to their study of O_2. Therefore, no metastable species have been included in our study.

2.3 Vibrationally excited molecules

The dissociative attachment cross section has been shown to depend on the extent of vibrational excitation of chlorine molecules in the discharge (Golovitskii, 2000; Ruf et al., 2004; Kolorenč and Horáček, 2006). Including vibrationally excited molecules should therefore be of much interest, given the importance of this particular cross section. Not until quite recently have cross sections for specific vibrational transitions become available (Ruf et al., 2004; Kolorenč and Horáček, 2006), making it possible for us to include vibrationally excited ground state chlorine molecules in the reaction set in the same manner as has been done in the nitrogen discharge (Thorsteinsson, 2008; Thorsteinsson and Gudmundsson, 2009).

3 Rate coefficients

The rate coefficient for an electron impact collision is obtained by integrating the cross section over an assumed Maxwellian distribution

$$k = \langle \sigma(v)v \rangle_v = 4\pi \int_0^\infty \sigma(v)v^3 f(v)dv \tag{1}$$

where σ is the collision cross section, v the electron velocity and

$$f(v) = \left(\frac{m_e}{2\pi e T_e} \right)^{3/2} \exp \left(-\frac{m_e v^2}{2e T_e} \right) \tag{2}$$

is the Maxwellian velocity distribution, m_e is the electron mass, e is the electron charge and T_e is the electron temperature. Using the relationship between the velocity and kinetic energy of a particle

$$\mathcal{E} = \frac{m_e v^2}{2e} \tag{3}$$

we find

$$f(\mathcal{E}) = \frac{2}{\sqrt{\pi}} \frac{1}{T_e^{3/2}} \exp \left(-\frac{\mathcal{E}}{T_e} \right) \tag{4}$$

to be the normalized Maxwellian electron energy distribution. Thus

$$k = \int_0^\infty \sigma(\mathcal{E}) \left(\frac{8e\mathrm{T_e}}{\pi m_e}\right)^{1/2} \frac{\mathcal{E}}{\mathrm{T_e}} \exp\left(-\frac{\mathcal{E}}{\mathrm{T_e}}\right) \frac{d\mathcal{E}}{\mathrm{T_e}} \tag{5}$$
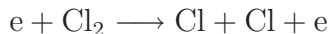
is the rate coefficient.

3.1 Electron collisions with molecular chlorine

Here we will discuss the cross sections and the resulting rate coefficients for collisions of electrons with molecular chlorine. For most of the processes, we will by default assume that the given cross sections apply to collisions with $Cl_2(v = 0)$, while the corresponding cross sections for collisions with $Cl_2(v > 0)$ will be obtained by reducing the threshold the appropriate multiple of the vibrational energy spacing of the chlorine molecule, 0.07 eV (Christophorou and Olthoff, 1999). This may not be accurate, but is an appropriate first approximation in the absence of proper information.

3.1.1 Electron impact dissociation of Cl_2

The total cross section for the dissociation of the chlorine molecule

$$e + Cl_2 \longrightarrow Cl + Cl + e$$

was measured by Cosby and Helm (1992), but since the results have not been properly published the data was taken from Christophorou and Olthoff (1999). Rescigno (1994) calculated the excitation cross sections for the five lowest-lying electronic states of Cl_2. The dissociation energy of Cl_2 is only about 2.5 eV, which is below the excitation energy of the lowest excited state of the molecule. All the excited states lead to dissociation. The cross sections were therefore summed up as an estimate of the total dissociation cross section. The measured and calculated dissociation cross sections are in relatively good agreement. Thus, preferring experimental data over calculations, we will use the cross section measured by Cosby and Helm (1992) as recommended by Christophorou and Olthoff (1999). The cross section is shown in figure 1. Assuming a Maxwellian electron energy distribution, the corresponding rate coefficient is given by

$$k_{\mathrm{diss,Cl_2}} = 6.67 \times 10^{-14} \mathrm{T_e}^{-0.10} \mathrm{e}^{-8.67/\mathrm{T_e}} \quad \mathrm{m^3/s}$$
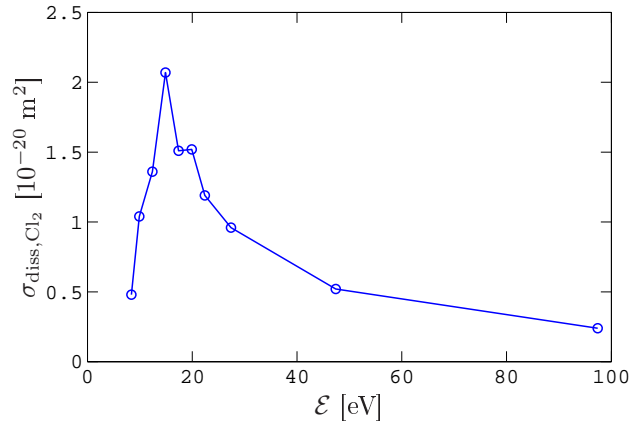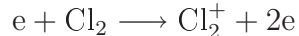
Figure 1: The cross section for electron impact dissociation of Cl_2 as measured by Cosby and Helm (1992) and recommended by Christophorou and Olthoff (1999).

3.1.2 Electron impact ionization of Cl_2

Electron impact ionization of the chlorine molecule in the ground state

$$e + Cl_2 \longrightarrow Cl_2^+ + 2e$$

has ionization potential of roughly 11.5 eV (Ralchenko et al., 2008).

The total electron impact ionization cross section for molecular chlorine was measured by Center and Mandl (1972), Kurepa and Belić (1978) and Stevie and Vasile (1981) and calculated by Joshipura and Limbachiya (2002). Furthermore, Christophorou and Olthoff (1999) reviewed the available cross sections for the total ionization of Cl_2, as well as some unpublished and almost unobtainable data available at the time, and recommended a cross section that is an average of two of the measured cross sections (Kurepa and Belić, 1978; Stevie and Vasile, 1981). The total ionization cross section is generally just a measure of the total positive-ion production and includes contributions of dissociative ionization, dissociative double ionization and polar dissociation. The partial cross section, specific to the formation of Cl_2^+ due to electron impact ionization of Cl_2, has been measured by Basner and Becker (2004) and calculated by Pal et al. (2003) and Ali and Kim (2005). Additionally, Calandra et al. (2000) measured the branching ratio versus electron energy of the various channels of electron impact ionization. There is

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a significant variation in the size and shape of the total cross section between the different measurements and calculations. The calculations of the partial cross sections suggest that the formation of Cl_2^+ dominates the total cross section (Pal et al., 2003; Ali and Kim, 2005), while the two measurements agree that Cl^+ production may account for roughly half of the total cross section, depending on energy (Calandra et al., 2000; Basner and Becker, 2004). Preferring the experimental data over the calculations, we will use the partial Cl_2^+ formation cross section measured by Basner and Becker (2004) as the basis for our rate constant, given by

$$k_{\mathrm{iz,Cl_2}} = 4.87 \times 10^{-14} \mathrm{T_e}^{0.50} \exp(-12.17/\mathrm{T_e}) \quad \mathrm{m^3/s}$$

when a Maxwellian-like electron energy distribution has been assumed. The cross section is given by the solid line in figure 2.
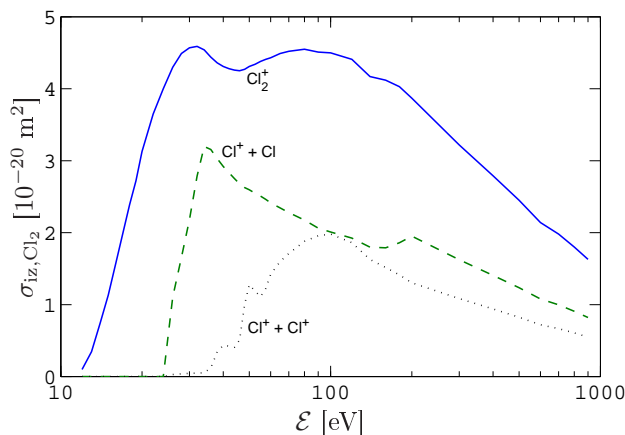

Figure 2: The partial cross sections for electron impact ionization of Cl_2. Solid line: direct ionization of Cl_2 (Basner and Becker, 2004), $\sigma_{\mathrm{iz,Cl_2}}$. Dashed line: dissociative single ionization of Cl_2, $\sigma_{\mathrm{diz_1,Cl_2}}$. Dotted line: dissociative double ionization of Cl_2, $\sigma_{\mathrm{diz_2,Cl_2}}$. The latter two cross sections were obtained by multiplying the branching ratio measurement of Calandra et al. (2000) for these channels with the direct ionization cross section of Basner and Becker (2004) (solid line).

The partial cross section for dissociative ionization

$$e + Cl_2 \longrightarrow Cl + Cl^+ + 2e$$

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was not determined specifically experimentally or theoretically until Calandra et al. (2000) measured the branching ratio of the total cross section (Cl^+/Cl_2^+). The partial dissociative ionization cross section was found to be almost as large as the direct ionization cross section (production of Cl_2^+). This result was supported by a later measurement of the absolute partial cross section by Basner and Becker (2004). However, Pal et al. (2003) found semi-empirically that the Cl^+ formation contributed much less to the total cross section than the Cl_2^+ formation. This result was later supported by the calculation of Ali and Kim (2005), who found that the partial cross section for the formation of Cl_2^+ was only marginally smaller than the total ionization cross section. Presuming the calculated partial cross sections are in error rather than the measured cross sections, we would prefer the absolute cross section measured by Basner and Becker (2004). However, since that cross section is for the total formation of Cl^+ by electron impact ionization of Cl_2, it includes a contribution from dissociative double ionization (formation of a pair of Cl^+). Calandra et al. (2000) determined the branching ratio for dissociative single ionization specifically, and we will therefore multiply it by the cross section used for non-dissociative ionization of Cl_2 to obtain the proper cross section. The cross section is shown by the dashed line in figure 2. The resulting rate coefficient for a Maxwellian-like electron energy distribution is given by

$$k_{\mathrm{diz_1},Cl_2} = 1.79 \times 10^{-13} \exp(-24.88/T_e) \quad \mathrm{m^3/s}$$

The partial cross section for dissociative double ionization
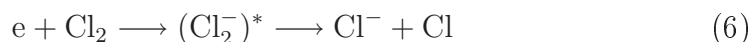
$$e + Cl_2 \longrightarrow Cl^+ + Cl^+ + 3e$$

has been determined only once by Calandra et al. (2000), who measured the branching ratio of the cross section rather than its absolute value. The reaction has a threshold of roughly 28.5 eV (an appearance energy of about 35 eV according to the branching ratio measurement) and is therefore not expected to have a large rate coefficient, although the cross section may be large at high energy. We will multiply the branching ratio given by Calandra et al. (2000) by the cross section chosen for the non-dissociative ionization of Cl_2 in order to obtain a cross section for the dissociative double ionization of

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Cl_2. The cross section is given by the dotted line in figure 2. The resulting rate coefficient for a Maxwellian-like electron energy distribution is given by

$$k_{\mathrm{diz_2,Cl_2}} = 1.46 \times 10^{-16} \mathrm{T_e}^{2.16} \exp(-21.42/\mathrm{T_e}) \quad \mathrm{m^3/s}$$

3.1.3 Dissociative attachment of electrons on Cl_2

Dissociative electron attachment on Cl_2,

$$\mathrm{e} + Cl_2 \longrightarrow (Cl_2^-)^* \longrightarrow Cl^- + Cl \qquad (6)$$

has a very low or no threshold energy. If the $(Cl_2^-)^*$ is in its first (unstable) $^2\Pi_g$ electronic level the first process is roughly resonant at zero electron energy, given that the electron affinity of Cl_2^- and the excitation energy of $Cl_2^-(^2\Pi_g)$ are about the same, ~ 2.5 eV (Christophorou and Olthoff, 1999). The cross section for the electron impact dissociative ionization thus exhibits a sharp peak near zero energy, or at about 0.05 eV (Ruf et al., 2004) (indicating the reaction is actually endothermic about this energy). The cross section has been measured (Kurepa and Belić, 1978; Tam and Wong, 1978; Feketeova et al., 2003; Ruf et al., 2004) and calculated (Golovitskii, 2000; Fabrikant et al., 2000; Ruf et al., 2004; Kolorenč and Horáček, 2006) in several studies, yielding results in a relatively good agreement. Furthermore, Christophorou and Olthoff (1999) recommended using the cross section measured by Kurepa and Belić (1978), but scaled upwards 30 % to give agreement with electron swarm data. Golovitskii (2000) showed that the total dissociative electron attachment cross section increased with increasing population of vibrationally excited chlorine molecules, $Cl_2(v > 0)$. This assessment was supported by Ruf et al. (2004) and Kolorenč and Horáček (2006) who calculated cross sections for dissociative electron attachment in collisions with chlorine molecules in various vibrational levels and found a significant increase in the peak value with increasing vibrational level, being 4–5 times larger for $v = 1$ compared to $v = 0$, for example. Neither study found a significant variation in the shape of the cross section with vibrational level of the reactant molecule. Most of the dissociative electron attachment cross sections are in relatively good agreement with the cross section recommended

by Christophorou and Olthoff (1999), in particular the relatively recent experimental and semi-empirical R-matrix study of the cross section by Ruf et al. (2004). Therefore, we will use this recommended cross section, the scaled-up measurement of Kurepa and Belić (1978), for the dissociative attachment of electrons on $Cl_2(v = 0)$ molecules at energies above 0.2 eV. We will use the cross section measured by Ruf et al. (2004) at lower energies, describing the behavior near zero energy in detail. For vibrationally excited reactants we will scale the cross sections according to Ruf et al. (2004), where the $v = 1 - 3$ cross sections are roughly 4.1, 8.8 and 13.5 times larger than the $v = 0$ cross section, respectively. The dissociative attachment cross sections are shown in figure 3. The resulting rate coefficients for a Maxwellian-like
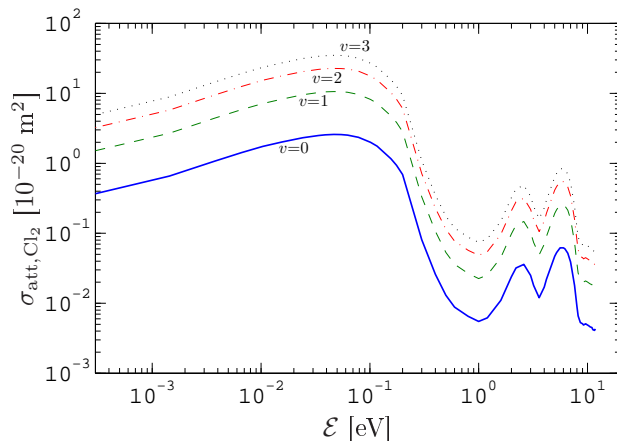

Figure 3: The cross section for electron impact dissociative attachment of $Cl_2(v = 0 - 3)$. The cross section denoted by $v = 0$ is compiled from the measurement of Ruf et al. (2004) at energies below 0.2 eV and from the cross section measured by Kurepa and Belić (1978), scaled upwards 30 % as recommended by Christophorou and Olthoff (1999), at higher energy. The cross sections for the $v = 1 - 3$ levels were obtained by multiplying the $v = 0$ cross section by 4.1, 8.8 and 13.5, respectively, as indicated by the calculations of Ruf et al. (2004).

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electron energy distribution are given by

$$
k_{\mathrm{att,Cl_2}} =
\begin{cases}
8.15 \times 10^{-16} \mathrm{T_e}^{-0.57} \exp(-1.02/\mathrm{T_e}) & \text{for } v = 0 \\
3.34 \times 10^{-15} \mathrm{T_e}^{-0.57} \exp(-1.01/\mathrm{T_e}) & \text{for } v = 1 \\
7.17 \times 10^{-15} \mathrm{T_e}^{-0.57} \exp(-1.02/\mathrm{T_e}) & \text{for } v = 2 \\
1.10 \times 10^{-14} \mathrm{T_e}^{-0.57} \exp(-1.01/\mathrm{T_e}) & \text{for } v = 3
\end{cases}
$$

in m^3/s. We noticed that the numerical value of the rate coefficient was heavily affected by the choice of the low energy behavior of the cross section. For example, if a zero cross section at zero energy was specified additionally for the cross section given by Christophorou and Olthoff (1999), whose lowest energy value was at at 0.05 eV, the resulting rate coefficient roughly doubled in its value compared to not doing so. Since the cross section peaks at very low energies, the Arrhenius form of the rate coefficient is not sufficient and the fit is not particularly accurate, especially at low energies. We found that by adding additional terms to the Arrhenius form the accuracy of the fit was substantially better, giving a good fit even when the rate coefficient was fit over a wider electron temperature, important for pulsed model studies. This more complex and accurate fit to the rate coefficient, valid in the electron temperature range $1 - 7$ V, is given by

$$
k'_{\mathrm{att,Cl_2}} =
\begin{cases}
10^{-16} \times (22.5\mathrm{T_e}^{-0.46}\mathrm{e}^{-2.82/\mathrm{T_e}} - 12.1\mathrm{e}^{-0.99/\mathrm{T_e}} + 6.54) & \text{for } v = 0 \\
10^{-15} \times (9.29\mathrm{T_e}^{-0.47}\mathrm{e}^{-2.83/\mathrm{T_e}} - 4.96\mathrm{e}^{-0.99/\mathrm{T_e}} + 2.70) & \text{for } v = 1 \\
10^{-15} \times (20.1\mathrm{T_e}^{-0.47}\mathrm{e}^{-2.83/\mathrm{T_e}} - 10.8\mathrm{e}^{-0.97/\mathrm{T_e}} + 5.92) & \text{for } v = 2 \\
10^{-15} \times (30.5\mathrm{T_e}^{-0.46}\mathrm{e}^{-2.82/\mathrm{T_e}} - 16.3\mathrm{e}^{-0.99/\mathrm{T_e}} + 8.81) & \text{for } v = 3
\end{cases}
$$

in m^3/s. This kind of treatment is not necessary for any of the other aforementioned or subsequent rate coefficients, since the normal Arrhenius form of the rate coefficient is sufficiently accurate for all the other processes, even down to 0.1 eV.

3.1.4 Electron impact polar dissociation of Cl$_2$

The cross section for polar dissociation

$$
\mathrm{e} + \mathrm{Cl_2} \longrightarrow \mathrm{Cl^-} + \mathrm{Cl^+} + \mathrm{e} \tag{7}
$$

was measured (as a part of a total negative ion formation cross section) by Kurepa and Belić (1978). Since the process has a roughly 11.9 eV threshold, they assumed the measured cross section for negative ion formation corresponded to polar dissociation above this energy. However, this cross section likely includes a contribution from dissociative attachment, in particular in the region $11 - 30$ eV where Kurepa and Belić (1978) in fact believed ion-pair formation had a smaller contribution to the cross section than dissociative attachment. Nevertheless, Christophorou and Olthoff (1999) recommended the use of this cross section after it had been adjusted upwards by 30 % as indicated by electron swarm studies. Golovitskii (2000) used the cross section measured by Kurepa and Belić (1978) to evaluate the dependence of dissociative attachment on the vibrational level population. To do this the cross section was represented as a sum of Gaussian curves, making it possible to minimize the overlap of polar dissociation and dissociative attachment. We will therefore use this cross section, or rather its vibrationally cold value ($T = 300$ K), for electron impact polar dissociation. The cross section for polar dissociation is shown in figure 4. The resulting rate coefficient for a
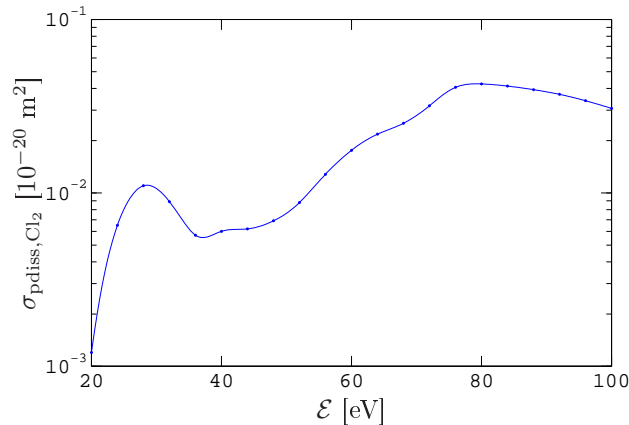

Figure 4: The cross section for electron impact polar dissociation as derived from the cross section of Kurepa and Belić (1978) by Golovitskii (2000).

Maxwellian-like electron energy distribution is given by

$$k_{\mathrm{pdiss,Cl_2}} = 3.45 \times 10^{-16} \mathrm{T_e}^{0.13} \exp(-19.70/\mathrm{T_e}) \quad \mathrm{m^3/s}$$

3.1.5 Electron impact vibrational excitation

There exist no direct measurements of the cross section for the vibrational excitation of ground state chlorine molecules,

$$e + Cl_2(v = 0) \longrightarrow Cl_2(v > 0) + e$$

or the vibrational excitation of vibrationally excited chlorine molecules,

$$e + Cl_2(v = j) \longrightarrow Cl_2(v > j) + e.$$

The total vibrational excitation cross section was estimated in the electron swarm studies by Rogoff et al. (1986) and Pinhão and Chouki (1995) (taken from Christophorou and Olthoff (1999)). Christophorou and Olthoff (1999) estimated the total vibrational cross section as well by subtracting the cross sections for elastic and the other inelastic processes from the total scattering cross section, for which experimental data was available. Ruf et al. (2004) calculated the cross section for the vibrational transitions $v = 0 \rightarrow 1 - 3$ and $v = 1 \rightarrow 2 - 4$ while Kolorenč and Horáček (2006) calculated the cross section for the transitions $v = 0 \rightarrow 1 - 4$ and $v = 1 \rightarrow 2 - 5$. The cross section calculated by Ruf et al. (2004) seem to be in a better agreement with the estimated total cross section of Christophorou and Olthoff (1999) and is given over a wider electron energy range than the vibrational excitation cross sections of Kolorenč and Horáček (2006). Therefore, we will use their cross sections for the vibrational transitions $v = 0 \rightarrow 1 - 3$ and $v = 1 \rightarrow 2 - 3$. The cross section for the vibrational transition $v = 2 \rightarrow 3$ is needed in order to complete the set of vibrational excitation cross sections. Since the peak values of the $v = 0 \rightarrow 1$ and $v = 1 \rightarrow 2$ cross sections are very similar (and for that matter the $v = 0 \rightarrow 2$ and $v = 1 \rightarrow 3$ peak values as well), we will assume the cross section for $v = 2 \rightarrow 3$ has the same shape and magnitude as the $v = 1 \rightarrow 2$ cross section. Ruf et al. (2004) only calculated partial cross sections for the various channels of each vibrational excitation. The sum of these partial cross sections is shown in figure 5. The resulting rate
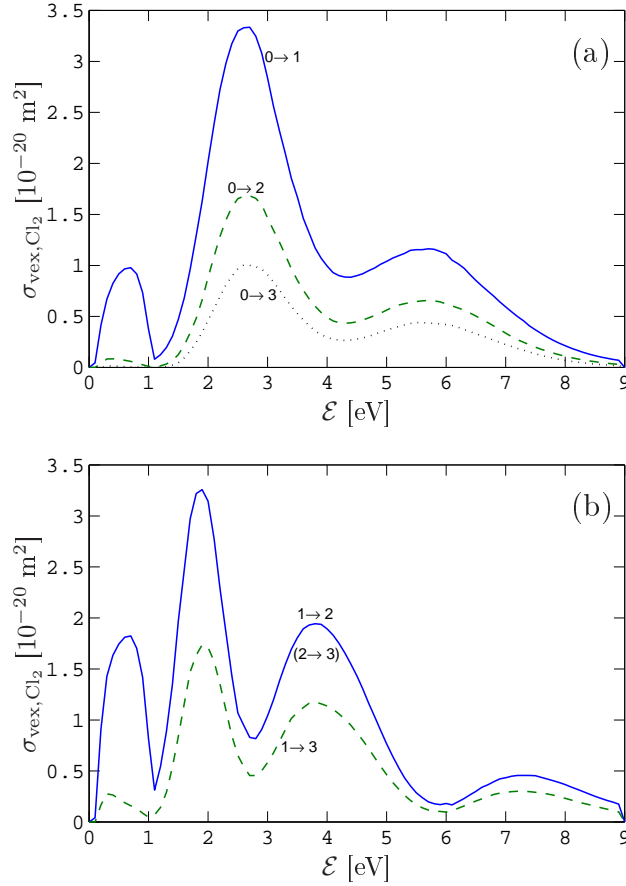
Figure 5: The cross sections for electron impact vibrational excitation of (a) $Cl_2(v = 0)$ and (b) $Cl_2(v > 0)$. The cross sections shown here represent a sum of the partial cross sections calculated by Ruf et al. (2004) for the various channels of each transition. The cross section for the $v = 2 \to 3$ transition was assumed to be identical to the $v = 1 \to 2$ cross section.

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coefficients for a Maxwellian-like electron energy distribution are given by

$$
k_{\text{vex,Cl}_2} = \begin{cases} 8.94 \times 10^{-14} \text{T}_{\text{e}}^{-1.14} \exp(-2.39/\text{T}_{\text{e}}) & \text{for } v = 0 \rightarrow 1 \\ 5.04 \times 10^{-14} \text{T}_{\text{e}}^{-1.17} \exp(-2.70/\text{T}_{\text{e}}) & \text{for } v = 0 \rightarrow 2 \\ 3.16 \times 10^{-14} \text{T}_{\text{e}}^{-1.17} \exp(-2.81/\text{T}_{\text{e}}) & \text{for } v = 0 \rightarrow 3 \\ 6.52 \times 10^{-14} \text{T}_{\text{e}}^{-1.10} \exp(-1.87/\text{T}_{\text{e}}) & \text{for } v = 1 \rightarrow 2 \\ 4.18 \times 10^{-14} \text{T}_{\text{e}}^{-1.14} \exp(-2.30/\text{T}_{\text{e}}) & \text{for } v = 1 \rightarrow 3 \\ 6.52 \times 10^{-14} \text{T}_{\text{e}}^{-1.10} \exp(-1.87/\text{T}_{\text{e}}) & \text{for } v = 2 \rightarrow 3 \end{cases}
$$

in m^3/s.

The cross sections for the corresponding superelastic deexcitation reactions will be obtained by the principle of detailed balancing. Since each vibrational level is assumed to have a unity degeneracy the detailed balancing procedure consists only of simple reduction of the cross section threshold about an appropriate multiple of the vibrational energy spacing of the Cl_2 molecule, 0.07 eV (Christophorou and Olthoff, 1999). The resulting rate coefficients for a Maxwellian electron energy distribution are given by

$$
k_{\text{vdex,Cl}_2} = \begin{cases} 8.94 \times 10^{-14} \text{T}_{\text{e}}^{-1.14} \exp(-2.32/\text{T}_{\text{e}}) & \text{for } v = 1 \rightarrow 0 \\ 5.04 \times 10^{-14} \text{T}_{\text{e}}^{-1.17} \exp(-2.56/\text{T}_{\text{e}}) & \text{for } v = 2 \rightarrow 0 \\ 3.15 \times 10^{-14} \text{T}_{\text{e}}^{-1.17} \exp(-2.59/\text{T}_{\text{e}}) & \text{for } v = 3 \rightarrow 0 \\ 6.31 \times 10^{-14} \text{T}_{\text{e}}^{-1.08} \exp(-1.76/\text{T}_{\text{e}}) & \text{for } v = 2 \rightarrow 1 \\ 6.31 \times 10^{-14} \text{T}_{\text{e}}^{-1.08} \exp(-1.76/\text{T}_{\text{e}}) & \text{for } v = 3 \rightarrow 2 \\ 4.19 \times 10^{-14} \text{T}_{\text{e}}^{-1.14} \exp(-2.16/\text{T}_{\text{e}}) & \text{for } v = 3 \rightarrow 1 \end{cases}
$$

in m^3/s.

3.1.6 Dissociative recombination of Cl_2^+

Electron impact dissociative recombination has been shown to be very important during the off-period in a pulsed nitrogen discharge (Thorsteinsson, 2008). The rate coefficient or cross section for dissociative recombination of of Cl_2^+,

$$
\text{e} + \text{Cl}_2^+ \longrightarrow \text{Cl} + \text{Cl}
$$

has never been measured or calculated according to Christophorou and Olthoff (1999) or Florescu-Mitchell and Mitchell (2006). As a result, the reaction was not included at all in a previous global model study of the pulsed chlorine discharge (Ashida and Lieberman, 1997). Subramonium (2003) estimated the rate coefficient to be $1 \times 10^{-13} T_e^{-0.5}$ m^3/s. Ono et al. (1994) assumed the rate coefficient for dissociative recombination of Ar$_2^+$, $9 \times 10^{-13} T_e^{-0.6}$ m^3/s, applied to dissociative recombination of Cl$_2^+$, presumably because of the similar mass and electron configuration of Ar and Cl, being side-by-side in the periodic table. However, these rate coefficients are likely an overestimation of the actual rate coefficient, being on the order of the dissociative recombination rate coefficients applicable when $T_e \sim 300$ K (Gudmundsson and Lieberman, 2004). Florescu-Mitchell and Mitchell (2006) reviewed the field of dissociative recombination, yielding no rate coefficients for halogens such as fluorine or chlorine. The $T_e = 300$ K values for C$_2^+$, N$_2^+$, O$_2^+$ and Ne$_2^+$ were all quite similar, or around 2×10^{-13} m^3/s. This indicates there is not much variation of the dissociative recombination rate coefficient for elements in the same period. Looking at the rate coefficients for the noble gases there is roughly a linear increase in the value at $T_e = 300$ K with increasing period, having a slope of approximately 7×10^{-13} m^3/s a period. To estimate the rate coefficient for the dissociative recombination of Cl$_2^+$, we will assume this trend will hold for higher electron temperatures and apply to the $T_e = 1$ eV values for N$_2^+$ and O$_2^+$, while assuming an electron temperature dependence as $T_e^{-1/2}$. The 1 eV rate coefficients for N$_2^+$ and O$_2^+$ are roughly 2×10^{-14} m^3/s (Thorsteinsson, 2008; Gudmundsson and Lieberman, 2004) and we will therefore estimate the Cl$_2^+$ dissociative recombination rate coefficient with

$$k_{\mathrm{DR,Cl}_2^+} = 9 \times 10^{-14} T_e^{-0.5} \quad \mathrm{m}^3/\mathrm{s}$$

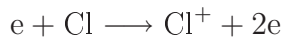which is an order of magnitude lower than the rate coefficient used by Ono et al. (1994).

3.2 Electron collisions with atomic chlorine

Since no excited chlorine molecules are included in the reaction set, the number of reactions involving collisions of electrons on atomic chlorine are very

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limited. Here we will discuss the cross sections for these processes and the resulting rate coefficients.

3.2.1 Electron impact ionization of the chlorine atom

Electron impact ionization of the chlorine atom in the ground state

$$e + Cl \longrightarrow Cl^+ + 2e$$

has an ionization potential of roughly 13.0 eV (Ralchenko et al., 2008).

Hayes et al. (1987) measured the total ionization cross section for positive ions. Calculations have also been made by Margreiter et al. (1994), Griffin et al. (1995), Joshipura and Limbachiya (2002), Bartlett and Stelbovics (2004) and Ali and Kim (2005), in addition to those mentioned in the review by Christophorou and Olthoff (1999). The calculations are for the most part in good agreement with the experimental cross section of Hayes et al. (1987). Christophorou and Olthoff (1999) recommend using the cross section measured by Hayes et al.. We will do this as well, but extend the cross section to higher energies by using the cross section calculated by Ali and Kim (2005) beyond 200 eV, which has roughly the same value at this high energy. The cross section is shown in figure 6. Assuming a Maxwellian-like electron energy distribution, the rate coefficient was then calculated as

$$k_{\mathrm{iz,Cl}} = 2.48 \times 10^{-14} \mathrm{T_e}^{0.62} \exp(-12.76/\mathrm{T_e}) \quad \mathrm{m^3/s}$$

3.2.2 Electron impact detachment of electrons from Cl$^-$

Electron detachment due to a collision of an electron with a negative ion,

$$e + Cl^- \longrightarrow Cl + 2e$$

is an important channel for the loss of the negative ion Cl$^-$. Nonetheless, only Fritioff et al. (2003) have measured the absolute cross section for the process. In the absence of any other data, we will use this cross section, shown by the solid line in figure 7, resulting in a rate coefficient for a Maxwellian-like electron energy distribution of

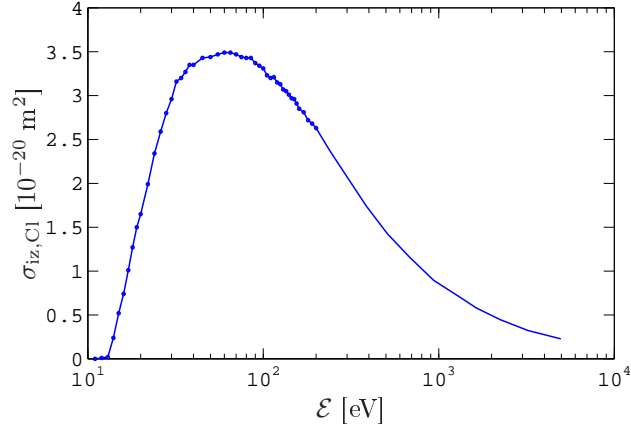$$k_{\mathrm{det,Cl^-}} = 2.33 \times 10^{-15} \mathrm{T_e}^{1.45} \exp(-2.48/\mathrm{T_e}) \quad \mathrm{m^3/s}$$

Figure 6: The cross section for electron impact ionization of the chlorine atom. The cross section is assembled from the cross section measured by Hayes et al. (1987) from threshold to 200 eV and from the cross section calculated by Ali and Kim (2005) at higher electron energies.
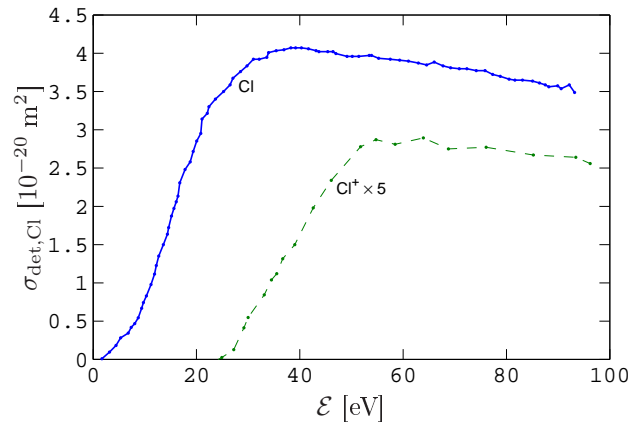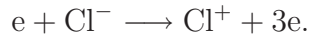

Figure 7: The cross sections for electron impact detachment of electrons from Cl$^-$ as measured by Fritioff et al. (2003). The single detachment cross section is given by the solid line, while the double detachment cross section has been multiplied by 5 and is represented by the dashed line.

Fritioff et al. (2003) also measured the cross section for the detachment of two electrons from Cl^-, forming a Cl^+,

$$e + Cl^- \longrightarrow Cl^+ + 3e.$$

This process has a high threshold and is therefore unlikely to be important for the overall chemistry. Nevertheless, it will be included in the reaction set. As can be seen from the dashed line in figure 7, the cross section has both a high threshold and a peak value over five times smaller than that of the single detachment cross section. The resulting rate coefficient for a Maxwellian-like electron energy distribution is given by,

$$k_{\mathrm{ddet,Cl^-}} = 3.38 \times 10^{-15} T_e^{0.75} \exp(-25.28/T_e) \quad m^3/s$$

3.3 Collisions of gas particles

3.3.1 Mutual neutralization of chlorine ions

Church and Smith (1978) reported measurements of the decay of ionization in positive/negative ion flowing afterglow plasmas (including chlorine), and obtained rate coefficients for various mutual neutralization reactions. For the reaction

$$Cl_2^+ + Cl^- \longrightarrow Products$$

they obtained the rate coefficient

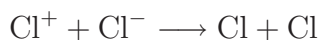$$5.0 \times 10^{-14} \qquad m^3/s$$

at a gas temperature of ~ 300 K. No other data seems to exists for this rate coefficient, other than the rough estimate of 1×10^{-13} m^3/s by Subramonium (2003). When the products are simply the parent neutrals of the ions, i.e. Cl_2 and Cl, the reaction is exothermic by about 7.9 eV. Since the lowest-lying electronic state of the atom has an excitation energy of roughly 8.9 eV, this energy is likely to be released as excitation to the molecule, which has several electronic states with excitation energies below 7.9 eV. However, since the dissociation energy of the molecule is only 2.5 eV, all the excited molecules are dissociative. Thus, we believe the reaction proceeds by

$$Cl_2^+ + Cl^- \longrightarrow Cl_2^* + Cl \longrightarrow Cl + Cl + Cl$$

which can be resonant and have a large rate coefficient if Cl_2^* is excited to an appropriate combination of electronic and vibrational levels. The cross sections for mutual neutralization reactions should depend inversely on the collision energy, according to the analysis by Lieberman and Lichtenberg (2005, p. 258). We will use this to estimate the dependence of the rate coefficient measured by Church and Smith (1978) on the gas temperature, resulting in

$$k_{Cl_2^+,Cl^-} = 5 \times 10^{-14}(300/T_g)^{1/2} \quad m^3/s.$$

Mutual neutralization of the positive and negative atomic ions,

$$Cl^+ + Cl^- \longrightarrow Cl + Cl$$

should have a large rate coefficient as well since the reaction is exothermic by 9.4 eV (Rogoff et al., 1986). We are not aware of any specific measurements or calculations for this rate coefficient. The rate coefficient is usually assumed to be equal to the mutual neutralization of Cl_2^+ and Cl^- (Rogoff et al., 1986; Ono et al., 1994; Lee and Lieberman, 1995; Kim et al., 2005; Hsu et al., 2006),

$$k_{Cl^+,Cl^-} = 5 \times 10^{-14}(300/T_g)^{1/2} \quad m^3/s.$$

We acknowledge that one of the product atoms will most likely be in an excited state, probably the 4s ^{4}P and 4s ^{2}P levels which have about 8.9 – 9.3 eV excitation energy. However, the neutral chlorine atom considered in the current study is assumed to be a collection of both ground state neutral atoms and neutral atoms in excited states, although the ground state atom is probably the dominating neutral atom because of the unusually high excitation energy of its lowest-lying excited energy levels.

3.3.2 Charge transfer

The charge transfer from the atomic ion Cl^+ to Cl_2 via the heavy particle collision

$$Cl^+ + Cl_2 \longrightarrow Cl + Cl_2^+$$

is exothermic by 1.5 eV and can therefore have a large rate coefficient. Španěl et al. (1993) measured the rate coefficient at $T_g = 300$ K in an ion flow tube
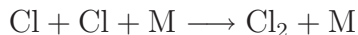
apparatus, resulting in the value

$$k_{\mathrm{ct,Cl^+}} = 5.4 \times 10^{-16} \quad \mathrm{m^3/s}$$

The extensive ion-molecule reaction review by Anicich (2003) did not mention any other values for this process. Since the gas temperature of the low pressure chlorine discharge can be expected to be significantly higher than the room temperature value associated with this rate coefficient, we would like to approximate the dependence of the rate coefficient on the gas temperature. The charge transfer rate coefficient for nitrogen is proportional to T_{g}^1 (Kossyi et al., 1992) while for oxygen it is proportional to $T_{\mathrm{g}}^{-1/2}$ (Eliasson and Kogelshatz, 1986). Thus, we cannot even know for sure whether the charge transfer rate coefficient for chlorine increases or decreases with increasing temperature. Therefore, in the absence of proper information thereof, we will assume this rate coefficient also applies at the higher gas temperatures expected in the low pressure inductive discharge in the current study.

The inverse reaction, the charge transfer from $\mathrm{Cl_2^+}$ to Cl, is endothermic by 1.5 eV and is only expected to occur at much higher temperatures.

3.3.3 Volume recombination of atoms

The association of two chlorine atoms can only occur if collisionally stabilized by a third particle. Although three particle reactions are unlikely to be important in the low pressure regime of inductive discharges, we will include the process just so that wall recombination is not the only channel for loss of atomic chlorine. The rate coefficient for the reaction

$$\mathrm{Cl + Cl + M \longrightarrow Cl_2 + M}$$

has been measured by several authors for M=$\mathrm{Cl_2}$. Boyd and Burns (1979) found a rate coefficient of 2.8×10^{-44} m^6/s at $T_{\mathrm{g}} = 300$ K for M=$\mathrm{Cl_2}$. Lloyd (1971) reviewed the literature for recombination of chlorine and fluorine, recommending a temperature dependent rate coefficient valid in the temperature range $T_{\mathrm{g}} = 200 - 500$ K,

$$k_{\mathrm{rec,Cl_2}} = 3.5 \times 10^{-45} \exp(810/T_{\mathrm{g}}) \quad \mathrm{m^6/s}$$

which is roughly double the value reported by Boyd and Burns (1979) at 300 K. We will use this value for M=Cl_2.

We were not able to find a determination of the rate coefficient for M=Cl. Subramonium (2003) used a value roughly 4 times smaller for M=Cl than for M=Cl_2. We will assume this assessment is correct, and lower our rate coefficient for M=Cl_2 by a factor of 4, resulting in

$$k_{\mathrm{rec,Cl}} = 8.75 \times 10^{-46} \exp(810/T_{\mathrm{g}}) \quad \mathrm{m^6/s}$$

for M=Cl.

4 Conclusion

The basic reaction set for the chlorine discharge is given in table 1. Aside from the rate coefficient discussed in section 3, we have also included rate coefficients for $Cl_2(v{>}0)$ reactants. These rate coefficients were calculated by reducing the energy threshold of the cross sections for the corresponding reactions with $Cl_2(v{=}0)$ reactants. The rate coefficients for electron impact collisions were calculated assuming a Maxwellian electron energy distribution and fit over the electron temperature range $1 - 7$ V. Although some of the cross sections used here have been taken from the review by Christophorou and Olthoff (1999), the availability of newer data has rendered many of their recommendations obsolete. The current reaction set has therefore been significantly revised compared to the reaction set used in the past by many modelling studies of chlorine discharges. It will for example be particularly interesting to see the effect of including vibrationally excited chlorine molecules in the reaction set, given the strong dependence of the dissociative attachment process on the vibrational excitation of the reactant. This will be the focal point of subsequent studies.

Acknowledgments

Table 1: The total reaction set for the chlorine discharge.

Reaction	Rate coefficient [m^3/s or m^6/s]	Ref.
e + Cl$_2$ $\rightarrow$ Cl + Cl + e	6.67×10^{-14} T$_e^{-0.10}$ e$^{-8.67/T_e}$	11
e + Cl$_2$ $\rightarrow$ Cl$_2^+$ + e + e	4.87×10^{-14} T$_e^{0.50}$ e$^{-12.17/T_e}$	5
e + Cl$_2$ $\rightarrow$ Cl + Cl$^+$ + e + e	1.79×10^{-13} e$^{-24.88/T_e}$	7, 5
e + Cl$_2$ $\rightarrow$ Cl$^+$ + Cl$^+$ + 3e	1.46×10^{-16} T$_e^{2.16}$ e$^{-21.42/T_e}$	7, 5
e + Cl$_2$ $\rightarrow$ Cl + Cl$^-$	$10^{-16} \times (22.5$T$_e^{-0.46}$ e$^{-2.82/T_e}$ - 12.1e$^{-0.99/T_e}$ + $6.54)$	28, 9
e + Cl$_2(v=1)$ $\rightarrow$ Cl + Cl$^-$	$10^{-15} \times (9.29$ T$_e^{-0.47}$ e$^{-2.83/T_e}$ - 4.96e$^{-0.99/T_e}$ + $2.70)$	44, 28, 9‡
e + Cl$_2(v=2)$ $\rightarrow$ Cl + Cl$^-$	$10^{-15} \times (20.1$ T$_e^{-0.47}$ e$^{-2.83/T_e}$ - 10.8e$^{-0.97/T_e}$ + $5.92)$	44, 28, 9‡
e + Cl$_2(v=3)$ $\rightarrow$ Cl + Cl$^-$	$10^{-15} \times (30.5$ T$_e^{-0.46}$ e$^{-2.82/T_e}$ - 16.3 e$^{-0.99/T_e}$ + $8.81)$	44, 28, 9‡
e + Cl$_2$ $\rightarrow$ Cl$^+$ + Cl$^-$ + e	3.45×10^{-16} T$_e^{0.13}$ e$^{-19.70/T_e}$	28, 18
e + Cl$_2$ $\rightarrow$ Cl$_2(v=1)$ + e	8.94×10^{-14} T$_e^{-1.14}$ e$^{-2.39/T_e}$	44
e + Cl$_2$ $\rightarrow$ Cl$_2(v=2)$ + e	5.04×10^{-14} T$_e^{-1.17}$ e$^{-2.70/T_e}$	44
e + Cl$_2$ $\rightarrow$ Cl$_2(v=3)$ + e	3.16×10^{-14} T$_e^{-1.17}$ e$^{-2.81/T_e}$	44
e + Cl$_2(v=1)$ $\rightarrow$ Cl$_2(v=2)$ + e	6.52×10^{-14} T$_e^{-1.10}$ e$^{-1.87/T_e}$	44
e + Cl$_2(v=1)$ $\rightarrow$ Cl$_2(v=3)$ + e	4.18×10^{-14} T$_e^{-1.14}$ e$^{-2.30/T_e}$	44
e + Cl$_2(v=2)$ $\rightarrow$ Cl$_2(v=3)$ + e	6.52×10^{-14} T$_e^{-1.10}$ e$^{-1.87/T_e}$	44
e + Cl$_2^+$ $\rightarrow$ Cl + Cl	9.00×10^{-14} T$_e^{-0.50}$	16, 21§
e + Cl $\rightarrow$ Cl$^+$ + e + e	2.48×10^{-14} T$_e^{0.62}$ e$^{-12.76/T_e}$	22, 1
e + Cl$^-$ $\rightarrow$ Cl + e + e	2.33×10^{-15} T$_e^{1.45}$ e$^{-2.48/T_e}$	17
e + Cl$^-$ $\rightarrow$ Cl$^+$ + 3e	3.38×10^{-15} T$_e^{0.75}$ e$^{-25.28/T_e}$	17
Cl$_2^+$ + Cl$^-$ $\rightarrow$ 3Cl	5.00×10^{-14} $(300/T_g)^{0.50}$	10
Cl$^+$ + Cl$^-$ $\rightarrow$ Cl + Cl	5.00×10^{-14} $(300/T_g)^{0.50}$	43, 10
Cl$_2$ + Cl$^+$ $\rightarrow$ Cl + Cl$_2^+$	5.40×10^{-16}	50
Cl$_2$ + Cl + Cl $\rightarrow$ Cl$_2$ + Cl$_2$	3.50×10^{-45} e$^{810/T_g}$	33
3Cl $\rightarrow$ Cl$_2$ + Cl	8.75×10^{-46} e$^{810/T_g}$	33, 46
e + Cl$_2(v=1)$ $\rightarrow$ Cl + Cl + e	5.96×10^{-14} T$_e^{-0.06}$ e$^{-8.40/T_e}$	11*
e + Cl$_2(v=2)$ $\rightarrow$ Cl + Cl + e	5.70×10^{-14} T$_e^{-0.04}$ e$^{-8.26/T_e}$	11*
e + Cl$_2(v=3)$ $\rightarrow$ Cl + Cl + e	5.25×10^{-14} T$_e^{-0.01}$ e$^{-8.05/T_e}$	11*
e + Cl$_2(v=1)$ $\rightarrow$ Cl$_2^+$ + e + e	4.61×10^{-14} T$_e^{0.52}$ e$^{-12.00/T_e}$	5*
e + Cl$_2(v=2)$ $\rightarrow$ Cl$_2^+$ + e + e	4.47×10^{-14} T$_e^{0.53}$ e$^{-11.88/T_e}$	5*
e + Cl$_2(v=3)$ $\rightarrow$ Cl$_2^+$ + e + e	4.44×10^{-14} T$_e^{0.54}$ e$^{-11.81/T_e}$	5*
e + Cl$_2(v=1)$ $\rightarrow$ Cl + Cl$^+$ + e + e	1.79×10^{-13} e$^{-24.81/T_e}$	7, 5*
e + Cl$_2(v=2)$ $\rightarrow$ Cl + Cl$^+$ + e + e	1.78×10^{-13} e$^{-24.74/T_e}$	7, 5*
e + Cl$_2(v=3)$ $\rightarrow$ Cl + Cl$^+$ + e + e	1.78×10^{-13} e$^{-24.67/T_e}$	7, 5*
e + Cl$_2(v=1)$ $\rightarrow$ Cl$^+$ + Cl$^+$ + 3e	1.45×10^{-16} T$_e^{2.16}$ e$^{-21.35/T_e}$	7, 5*
e + Cl$_2(v=2)$ $\rightarrow$ Cl$^+$ + Cl$^+$ + 3e	1.45×10^{-16} T$_e^{2.16}$ e$^{-21.28/T_e}$	7, 5*
e + Cl$_2(v=3)$ $\rightarrow$ Cl$^+$ + Cl$^+$ + 3e	1.44×10^{-16} T$_e^{2.16}$ e$^{-21.21/T_e}$	7, 5*
e + Cl$_2(v=1)$ $\rightarrow$ Cl$^+$ + Cl$^-$ + e	3.44×10^{-16} T$_e^{0.13}$ e$^{-19.63/T_e}$	28, 18*
e + Cl$_2(v=2)$ $\rightarrow$ Cl$^+$ + Cl$^-$ + e	3.43×10^{-16} T$_e^{0.13}$ e$^{-19.56/T_e}$	28, 18*
e + Cl$_2(v=3)$ $\rightarrow$ Cl$^+$ + Cl$^-$ + e	3.41×10^{-16} T$_e^{0.13}$ e$^{-19.49/T_e}$	28, 18*
e + Cl$_2(v=1)$ $\rightarrow$ Cl$_2$ + e	8.94×10^{-14} T$_e^{-1.14}$ e$^{-2.32/T_e}$	44†
e + Cl$_2(v=2)$ $\rightarrow$ Cl$_2$ + e	5.04×10^{-14} T$_e^{-1.17}$ e$^{-2.56/T_e}$	44†
e + Cl$_2(v=3)$ $\rightarrow$ Cl$_2$ + e	3.15×10^{-14} T$_e^{-1.17}$ e$^{-2.59/T_e}$	44†
e + Cl$_2(v=2)$ $\rightarrow$ Cl$_2(v=1)$ + e	6.31×10^{-14} T$_e^{-1.08}$ e$^{-1.76/T_e}$	44†
e + Cl$_2(v=3)$ $\rightarrow$ Cl$_2(v=2)$ + e	6.31×10^{-14} T$_e^{-1.08}$ e$^{-1.76/T_e}$	44†
e + Cl$_2(v=3)$ $\rightarrow$ Cl$_2(v=1)$ + e	4.19×10^{-14} T$_e^{-1.14}$ e$^{-2.16/T_e}$	44†

*Obtained by reducing the threshold of the cross section given in the cited reference, $\mathcal{E}' = \mathcal{E} - \mathcal{E}_a$

†Obtained by applying the principle of detailed balancing on the cross section given in the cited reference.

‡Magnitude of cross section changed from what given in the cited reference (see text).

§Estimated from similar rate coefficients given in the cited references (see text).

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