The rate coefficients for the collisional energy loss of the chlorine discharge

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by

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Abstract

The rate coefficients for electron impact excitation, electron impact ionization and elastic scattering of electrons for a chlorine processing discharge are reviewed. 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. The rate coefficients are then used to evaluate the collisional energy loss per electron-ion pair created.
1 Introduction

Most processing discharges are molecular and electronegative. The volume averaged global model for low pressure high density discharges was developed by Lieberman and Gottscho (1994) for noble gases and extended to molecular gases by Lee et al. (1994) and Lee and Lieberman (1995). The global model for oxygen was later further developed to include more species and reactions (Patel, 1998; Gudmundsson et al., 2001; Gudmundsson and Thorsteinsson, 2007). Volume averaged (global) models of the chlorine discharge have been developed (Meeks and Shon, 1995; Lee and Lieberman, 1995; Lee et al., 1996, 1997). Chlorine is an electronegative diatomic gas and is widely used in plasma etching of semiconductors, in particular silicon. Although chlorine has not been as well studied as the oxygen discharge, for example, there exist reviews for the data available in the literature (Morgan, 1992; Christophorou and Olthoff, 1999). In the global model, the reaction rate coefficients for electron collisions are calculated by integrating the collision cross sections over a Maxwellian electron energy distribution (Lieberman and Gottscho, 1994; Lee and Lieberman, 1995).

The main purpose of this work is to review the rate coefficients that are needed to evaluate the collisional energy loss per electron-ion pair created for the chlorine atom and the chlorine molecule. The rate coefficients were calculated assuming Maxwellian-like electron energy distribution and fit over the electron temperature range $1 - 7 \text{ V}$. Throughout the text we use the roman typeface symbol $T$ for the voltage equivalent of the temperature. An important quantity used in the global model is the collisional energy loss per electron-ion pair created $\mathcal{E}_c(T_e)$, which is defined as

$$\mathcal{E}_c = \mathcal{E}_{iz} + \sum_{i} \mathcal{E}_{\text{ex},i} \frac{k_{\text{ex},i}}{k_{iz}} + \frac{k_{\text{el}}}{k_{iz}} \frac{3m_e}{m_i} T_e$$  \hspace{1cm} (1)

where $\mathcal{E}_{iz}$ is the ionization energy, $\mathcal{E}_{\text{ex},i}$ is the threshold energy for the $i$-th excitation process, $k_{iz}$ is the ionization rate coefficient, $k_{\text{ex},i}$ is the rate coefficient for the $i$-th excited state and $k_{el}$ is the elastic rate coefficient. Thus the terms on the right hand side account for the loss of electron energy due to ionization, excitation, and elastic (polarization) scattering against neutral atoms.
2 Rate coefficients

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

$$k = \langle \sigma(v)v \rangle_v = 4\pi \int_0^\infty \sigma(v)v^3 f(v) dv$$  \hspace{1cm} (2)

where $\sigma$ is the collision cross section, $v$ the electron velocity and

$$f(v) = \left( \frac{m_e}{2\pi eT_e} \right)^{3/2} \exp \left( -\frac{m_e v^2}{2eT_e} \right)$$  \hspace{1cm} (3)

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

$$\mathcal{E} = \frac{m_e v^2}{2e}$$  \hspace{1cm} (4)

we find

$$f(\mathcal{E}) = \frac{2}{\sqrt{\pi}} \frac{1}{T_e^{3/2}} \exp \left( -\frac{\mathcal{E}}{T_e} \right)$$  \hspace{1cm} (5)

to be the normalized Maxwellian electron energy distribution. Thus

$$k = \int_0^\infty \sigma(\mathcal{E}) \left( \frac{8eT_e}{\pi m_e} \right)^{1/2} \frac{\mathcal{E}}{T_e} \exp \left( -\frac{\mathcal{E}}{T_e} \right) \frac{d\mathcal{E}}{T_e}$$  \hspace{1cm} (6)

is the rate coefficient.

3 The chlorine atom

3.1 Excitation

The electron impact excitation has been surprisingly poorly studied for the chlorine atom. Ganas (1988) calculated the cross sections for several excitations from the ground state atom using a Born approximation and LS coupling. The author did not expect the cross sections to have a better accuracy than 20 %. Griffin et al. (1995) calculated the cross sections for few transitions from the ground state atom with the R-matrix method, but since
Figure 1: The cross sections for electron impact excitation of the chlorine atom calculated by Ganas (1988). (a) The excitations to the 4s, 4p, 3d and 4d levels and (b) the excitations to the 5s, 5p, 6s and 5d levels.
the results relied heavily on the number of states included, the cross sections are not reliable (Christophorou and Olthoff, 1999). Therefore, we will use the cross sections calculated by Ganas (1988) that are shown in figure 1. The excitation rate coefficients used for the calculation of the collisional energy loss of atomic chlorine were calculated by integrating the cross sections over an assumed Maxwellian electron energy distribution and fit over the electron temperature range 1 – 7 V, as described in section 2. The threshold energies for the excited states were extracted from energy level values given by Radziemski and Kaufman (1969). The rate coefficients for the excited states are given in table 1 along with the corresponding threshold energies.

### 3.2 Ionization

The ionization energy for chlorine atoms is $E_{iz} = 12.97$ eV (Lias, 2005). Hayes et al. (1987) measured the total ionization cross section for positive ions. Calculations have also been made by Margeiter et al. (1994), Griffen 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 2. Assuming a Maxwellian-like electron energy distribution, the rate coefficient was then calculated as

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

### 3.3 Elastic scattering

No experimental data exists for the elastic electron scattering of the chlorine atom. The cross section has been calculated in a few studies (Robinson and Geltman, 1967; Fabrikant, 1994; Griffin et al., 1995; Saha, 1996). The calculations were compared and shown to be in a reasonably good agreement
Figure 2: 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.

in the review of Christophorou and Olthoff (1999), although no suggestion for the cross section was given. Furthermore, Griffin et al. (1995) mentioned an unpublished calculation of the cross section that was reportedly in a good agreement with their cross section at high energy, but somewhat lower at low energy. Since the cross section calculated by Fabrikant (1994) was in agreement with this and was also focused at lower electron energy than the other calculations, we will use the cross section from $\sim 0$ eV – 0.4 eV. For the electron energy range 0.4 – 16 eV we will use the cross section calculated by Griffin et al. (1995). The resulting cross section is shown in figure 3 and the corresponding rate coefficient, assuming a Maxwellian-like electron energy distribution, is given

$$8.34 \times 10^{-13} T_e^{-0.38} \exp(-3.54/T_e) \text{ m}^3/\text{s}$$
Figure 3: The cross section for elastic scattering of electrons due to collisions with chlorine atoms. The cross section is compiled from the cross section calculated by Fabrikant (1994) at energy below 0.4 eV and from the cross section calculated by Griffin et al. (1995) at higher energy.

Table 1: The rate coefficients, calculated assuming a Maxwellian-like electron energy distribution, for electron collisions with chlorine atoms leading to collisional electron energy loss.

<table>
<thead>
<tr>
<th>Final state</th>
<th>Threshold [eV]</th>
<th>Rate coefficient [m^3/s]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4s</td>
<td>9.1</td>
<td>$1.16 \times 10^{-14} T_e^{0.12} \exp(-9.58/T_e)$</td>
<td>9</td>
</tr>
<tr>
<td>4p</td>
<td>10.5</td>
<td>$9.66 \times 10^{-14} T_e^{-0.33} \exp(-11.01/T_e)$</td>
<td>9</td>
</tr>
<tr>
<td>3d</td>
<td>11.2</td>
<td>$1.63 \times 10^{-14} T_e^{0.18} \exp(-10.24/T_e)$</td>
<td>9</td>
</tr>
<tr>
<td>5s</td>
<td>11.4</td>
<td>$3.28 \times 10^{-15} \exp(-10.48/T_e)$</td>
<td>9</td>
</tr>
<tr>
<td>5p</td>
<td>11.8</td>
<td>$2.53 \times 10^{-14} T_e^{-0.30} \exp(-12.12/T_e)$</td>
<td>9</td>
</tr>
<tr>
<td>4d</td>
<td>12.0</td>
<td>$8.99 \times 10^{-15} T_e^{0.14} \exp(-11.22/T_e)$</td>
<td>9</td>
</tr>
<tr>
<td>6s</td>
<td>12.1</td>
<td>$1.34 \times 10^{-15} \exp(-10.75/T_e)$</td>
<td>9</td>
</tr>
<tr>
<td>5d</td>
<td>12.4</td>
<td>$5.50 \times 10^{-15} T_e^{0.10} \exp(-12.27/T_e)$</td>
<td>9</td>
</tr>
<tr>
<td>Ionization</td>
<td>13.0</td>
<td>$2.48 \times 10^{-14} T_e^{0.62} \exp(-12.76/T_e)$</td>
<td>1, 14</td>
</tr>
<tr>
<td>Elastic scattering $(3m_e/m_C)T_e$</td>
<td>$8.34 \times 10^{-13} T_e^{-0.38} \exp(-3.54/T_e)$</td>
<td>8, 11</td>
<td></td>
</tr>
</tbody>
</table>
4 The chlorine molecule

4.1 Excitation

Since all chlorine molecules in low-lying electronic states above the ground state are dissociative, it is understandable that no experimental data exists for the excitation to specific electronic levels of the molecule. The total dissociation cross section measured by Cosby and Helm (1992) (given by Christophorou and Olthoff (1999)) could serve as a total excitation cross section, although the excitation is not to a specific excited state with a specific threshold energy. Rogoff et al. (1986) and Pinhão and Chouki (1995) (see Christophorou and Olthoff (1999)) used Boltzmann calculations to calculate cross sections for the excitation to various levels or a combination of electron levels. Rescigno (1994) calculated the cross sections for electron impact excitation to each of the four lowest-lying electronic states, as well as for the excitation to each of the two non-dissociative $^1\Pi_u$ and $^1\Sigma_u^+$ Rydberg levels. The sum of the dissociative level excitation cross sections was in reasonably good agreement with the aforementioned measurement of the total dissociation cross section. Therefore, we will use the cross sections calculated by Rescigno (1994) that are shown in figure 4 for the electron impact excitation of Cl$_2$. The threshold energies for the excited states were measured by Peyerimhoff and Buentink (1981) and later revised and recommended by Christophorou and Olthoff (1999). The threshold energies and the rate coefficients for the excited states, calculated assuming a Maxwellian electron energy distribution, are listed in table 2.

The total electron impact vibrational excitation cross section for the chlorine molecule 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

8
Figure 4: The cross sections calculated by Rescigno (1994) for electron impact excitation to (a) the dissociative levels $1^3\Pi_u$, $1^1\Pi_u$, $1^3\Pi_u$, $1^1\Pi_g$ and $1^3\Sigma_u^+$ and (b) the non-dissociative Rydberg levels $2^1\Pi_u$ and $1^3\Sigma_u^+$. 
\[ v = 0 \rightarrow 1 - 4 \text{ and } v = 1 \rightarrow 2 - 5. \] 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 Kolorenek and Horacek (2006). We will therefore use their cross sections for the transitions from the \( v = 0 \) state to \( v = 1 - 3 \) in the calculation of the collisional energy loss. 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 coefficients for a Maxwellian electron energy distribution are shown in table 2. The vibrational energy spacing of \( \text{Cl}_2 \) is roughly 0.07 eV according to Christophorou and Olthoff (1999), which will be used to assign threshold energies to each of the vibrational excitations.

![Graph](image.png)

Figure 5: The cross sections for electron impact vibrational excitation of the chlorine molecule. 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.

### 4.2 Ionization

The ionization energy of molecular chlorine is \( \mathcal{E}_{iz} = 11.5 \text{ eV} \) (Lias, 2005). The total electron impact ionization cross section for molecular chlorine was measured by Center and Mandl (1972), Kurepa and Belic (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 for the formation of electron – Cl$_2^+$ ion pair due to an electron impact with 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 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

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

when a Maxwellian-like electron energy distribution has been assumed. The cross section is shown in figure 6.

4.3 Elastic scattering

Rescigno (1994) calculated the total elastic electron scattering cross section for the chlorine molecule. Gote and Ehrhardt (1995) measured the differential cross sections for elastic scattering. Kutz and Meyer (1995) derived the integral cross section from these differential cross sections and compared the result to their calculation of the rotational scattering cross section, largely
believed to be composed of elastic scattering. Christophorou and Olothoff (1999) reviewed the available data, suggesting a cross section composed of a fit to the cross section calculated by Rescigno (1994) and the cross section measured by Gote and Ehrhardt (1995). Makochehanwa et al. (2003) measured the total scattering cross section for the chlorine molecule and derived a theoretical estimate of the elastic scattering cross section. The agreement with the cross section suggested by Christophorou and Olothoff (1999) was good. Being given over a wider electron energy range, we will therefore use the cross section suggested by Christophorou and Olothoff (1999) for elastic scattering of electrons from the chlorine molecule that is shown in figure 7. The resulting rate coefficient for a Maxwellian-like electron energy distribution is given by

$$k_{el,Cl_2} = 1.96 \times 10^{-13} T_e^{0.54} \exp(-0.90/T_e) \text{ m}^3/\text{s}$$
Figure 7: The cross section for the elastic scattering of electrons due to collisions with chlorine molecules as suggested by Christophrourou and Olthoff (1999). The suggested cross section is a fit to the cross sections calculated by Rescigno (1994) and measured by Gote and Ehrhardt (1995).

Table 2: The rate coefficients, calculated assuming a Maxwellian-like electron energy distribution, for electron collisions with chlorine molecules leading to collisional electron energy loss.

<table>
<thead>
<tr>
<th>Final state</th>
<th>Threshold [eV]</th>
<th>Rate coefficient [m$^3$/s]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1^3\Pi_u$</td>
<td>3.24</td>
<td>$1.14 \times 10^{-14} \exp(-5.32/T_e)$</td>
<td>34</td>
</tr>
<tr>
<td>$1^3\Pi_u$</td>
<td>4.04</td>
<td>$1.27 \times 10^{-14} T_e^{-0.20} \exp(-5.87/T_e)$</td>
<td>34</td>
</tr>
<tr>
<td>$1^3\Pi_u$</td>
<td>6.23</td>
<td>$3.66 \times 10^{-15} T_e^{0.24} \exp(-6.63/T_e)$</td>
<td>34</td>
</tr>
<tr>
<td>$1^3\Sigma_u^+$</td>
<td>6.86</td>
<td>$2.67 \times 10^{-15} T_e^{0.10} \exp(-8.27/T_e)$</td>
<td>34</td>
</tr>
<tr>
<td>$1^3\Pi_u$</td>
<td>6.80</td>
<td>$6.02 \times 10^{-15} T_e^{0.05} \exp(-6.89/T_e)$</td>
<td>34</td>
</tr>
<tr>
<td>$2^1\Sigma_u^+$</td>
<td>9.22</td>
<td>$7.59 \times 10^{-15} T_e^{0.12} \exp(-11.20/T_e)$</td>
<td>34</td>
</tr>
<tr>
<td>$1^3\Pi_u$</td>
<td>9.32</td>
<td>$2.82 \times 10^{-15} T_e^{-0.07} \exp(-12.11/T_e)$</td>
<td>34</td>
</tr>
<tr>
<td>$v = 1$</td>
<td>0.07</td>
<td>$8.94 \times 10^{-14} T_e^{-1.14} \exp(-2.39/T_e)$</td>
<td>37</td>
</tr>
<tr>
<td>$v = 2$</td>
<td>0.14</td>
<td>$5.04 \times 10^{-14} T_e^{-1.17} \exp(-2.70/T_e)$</td>
<td>37</td>
</tr>
<tr>
<td>$v = 3$</td>
<td>0.21</td>
<td>$3.16 \times 10^{-14} T_e^{-1.17} \exp(-2.81/T_e)$</td>
<td>37</td>
</tr>
<tr>
<td>Ionization</td>
<td>11.5</td>
<td>$4.87 \times 10^{-14} T_e^{0.50} \exp(-12.17/T_e)$</td>
<td>3</td>
</tr>
<tr>
<td>Elastic scattering $(3m_e/m_{Cl_2})T_e$</td>
<td>$1.96 \times 10^{-13} T_e^{0.54} \exp(-0.90/T_e)$</td>
<td>34, 10, 6</td>
<td></td>
</tr>
</tbody>
</table>
5 The collisional energy loss

The collisional energy loss per electron-ion pair created $\mathcal{E}_e$, as a function of the electron temperature $T_e$, is shown in figure 8 for atomic and molecular chlorine. At very low electron temperatures, elastic collisions are the dominant contributor to the collisional energy loss but become significantly less important with rising temperature. At high electron temperatures, the collisional energy losses approach the ionization energies of the chlorine atom and the chlorine molecule, being roughly 16 V and 12.25 V at a 100 V electron temperature, respectively. For molecular gases, additional energy losses include excitations of vibrational and rotational energy levels, molecular dissociation, etc. Thus, below the threshold of these processes, or below about 2 eV, the molecular energy loss becomes larger than the atomic energy loss.

![Graph](image)

Figure 8: The collisional energy loss per electron-ion pair created $\mathcal{E}_e$ as a function of the electron temperature $T_e$ for the chlorine atom and the chlorine molecule.
6 Conclusion

We have reviewed the rate coefficients and the threshold energies of the processes that contribute to the collisional energy loss of both the chlorine atom and the chlorine molecule. Only a handful of studies exist for the electron impact excitation of either the chlorine molecule or atom. However, the electron impact ionization of both the species is well studied and the cross sections can be considered to be relatively accurate. Similar applies to the elastic scattering cross sections since the few available studies are for the most part in good agreement. Using the chosen set of cross sections, we have evaluated the collisional energy loss of the chlorine atom and molecule. The atomic energy loss is larger at energies above 2 eV while the molecular energy loss is larger at lower energies.

Acknowledgments

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