On the reaction rates in the low pressure chlorine discharge

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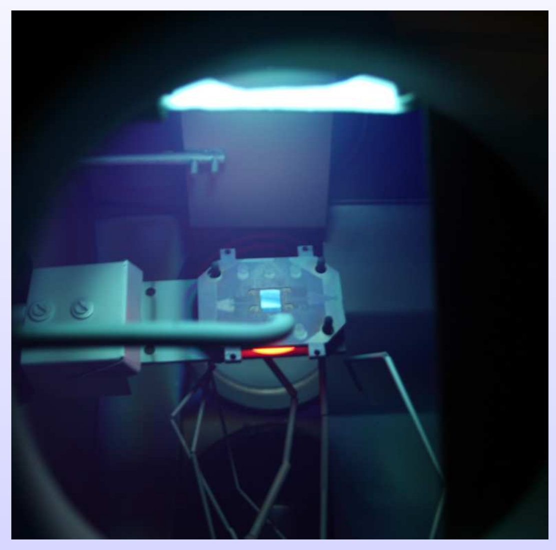

The global (volume averaged) model

- A global (volume averaged) model is applied to study a low pressure (1 – 100 mTorr) high density chlorine discharge in the steady state (Thorsteinsson and Gudmundsson, 2009).
- In addition to electrons we 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^+.
- Electrons are assumed to have a Maxwellian-like energy distribution in the range 1 – 7 V.
- The gas temperature is dependent on both power and pressure as measured by Donnelly and Malyshev (2000).
- The wall recombination coefficient γ_{rec} is dependent on the chlorine dissociation fraction (Stafford et al., 2009).
- The collisional energy loss per electron-ion pair created is defined as

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

where $\mathcal{E}_{iz}$ is the ionization energy, $\mathcal{E}_{ex,i}$ is the threshold energy and $k_{ex,i}$ is the rate coefficient for the i-th excitation process and k_{iz} is the ionization rate coefficient for single step ionization.

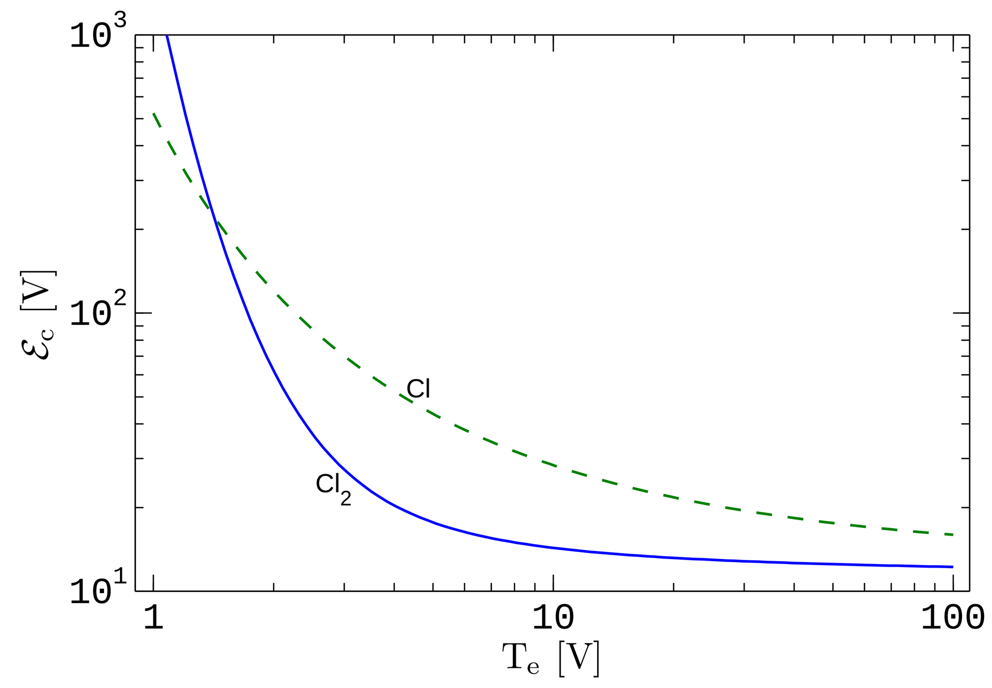

Figure 1: The collisional energy loss per electron-ion pair created $\mathcal{E}_c$ as a function of the electron temperature T_e for the chlorine atom and the chlorine molecule.

Results and discussion

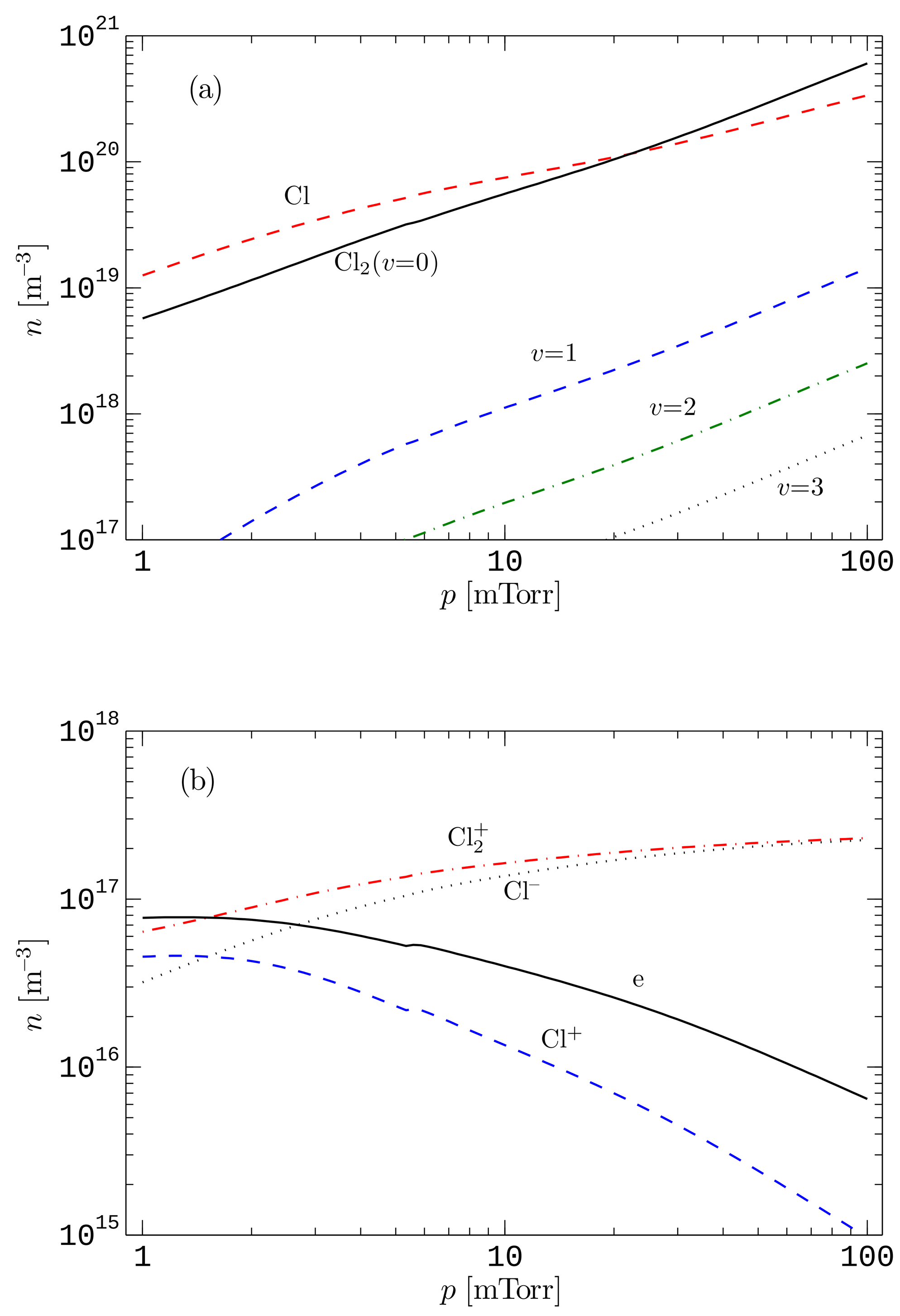

Figure 2: The density of (a) neutral chlorine species and (b) charged chlorine species versus discharge pressure at $P_{abs} = 323$ W, $Q = 100$ sccm, $R = 18.5$ cm and $L = 20$ cm.

- At low pressure the atomic chlorine Cl is the dominant discharge particle, whereas the chlorine molecule Cl_2 has a larger density at pressures above 20 mTorr.
- The dissociation fraction, $[Cl]/n_g$, varies from nearly 70 % at 1 mTorr to about 35 % at 100 mTorr.
- The vibrationally excited molecules $Cl_2(v > 0)$ have a density at least a factor of 40 smaller than the ground state $Cl_2(v = 0)$ density.
- Despite the apparently atomic nature of the neutral particles, the density of the atomic ion Cl^+ is always much smaller than the Cl_2^+ density, decreasing with pressure.

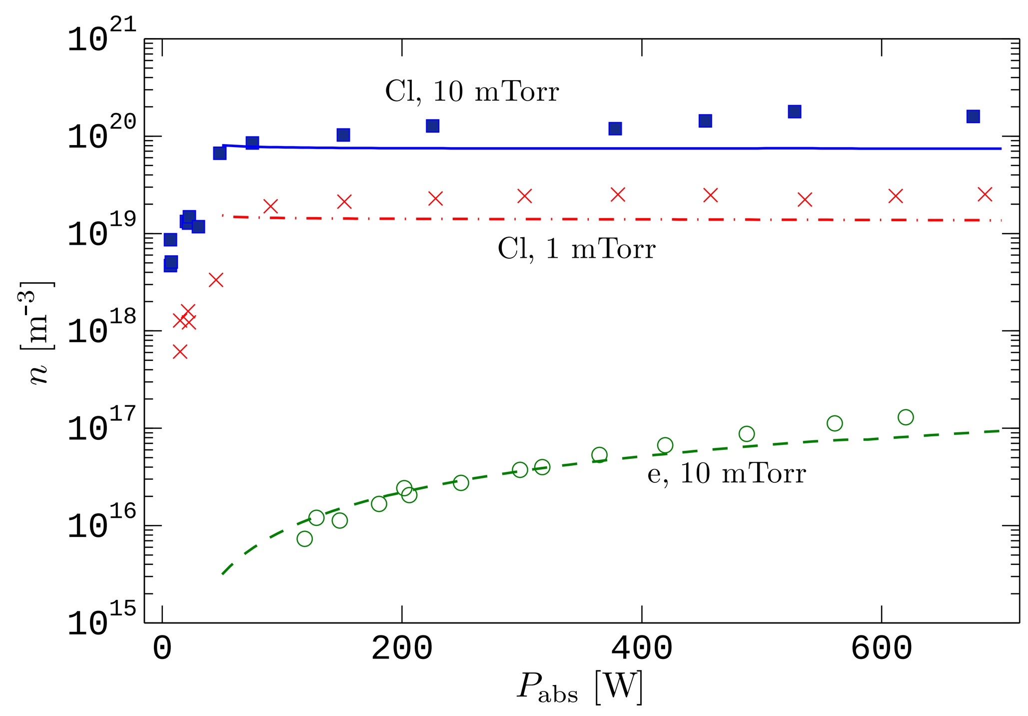

Figure 3: Model calculations of the atomic chlorine density at 10 and 1 mTorr (— and –·–) and the electron density at 10 mTorr (– –) versus absorbed power compared to measurements (Malyshev and Donnelly, 2000, 2001) (■, ×, ○, respectively) at $Q = 100$ sccm (20 sccm at 1 mTorr), $R = 18.5$ cm and $L = 20$ cm. A power coupling efficiency of 75 % was assumed for the measurements, i.e. $P_{abs}/P_{rf} = 0.75$.

- We compare the calculated Cl atom density at 1 and 10 mTorr and the calculated electron density at 10 mTorr to the measurements of Malyshev and Donnelly (2000, 2001).
- The calculated density of atomic chlorine is in a very good agreement with the measured data at both 1 and 10 mTorr.
- The agreement with the measured electron density is excellent.

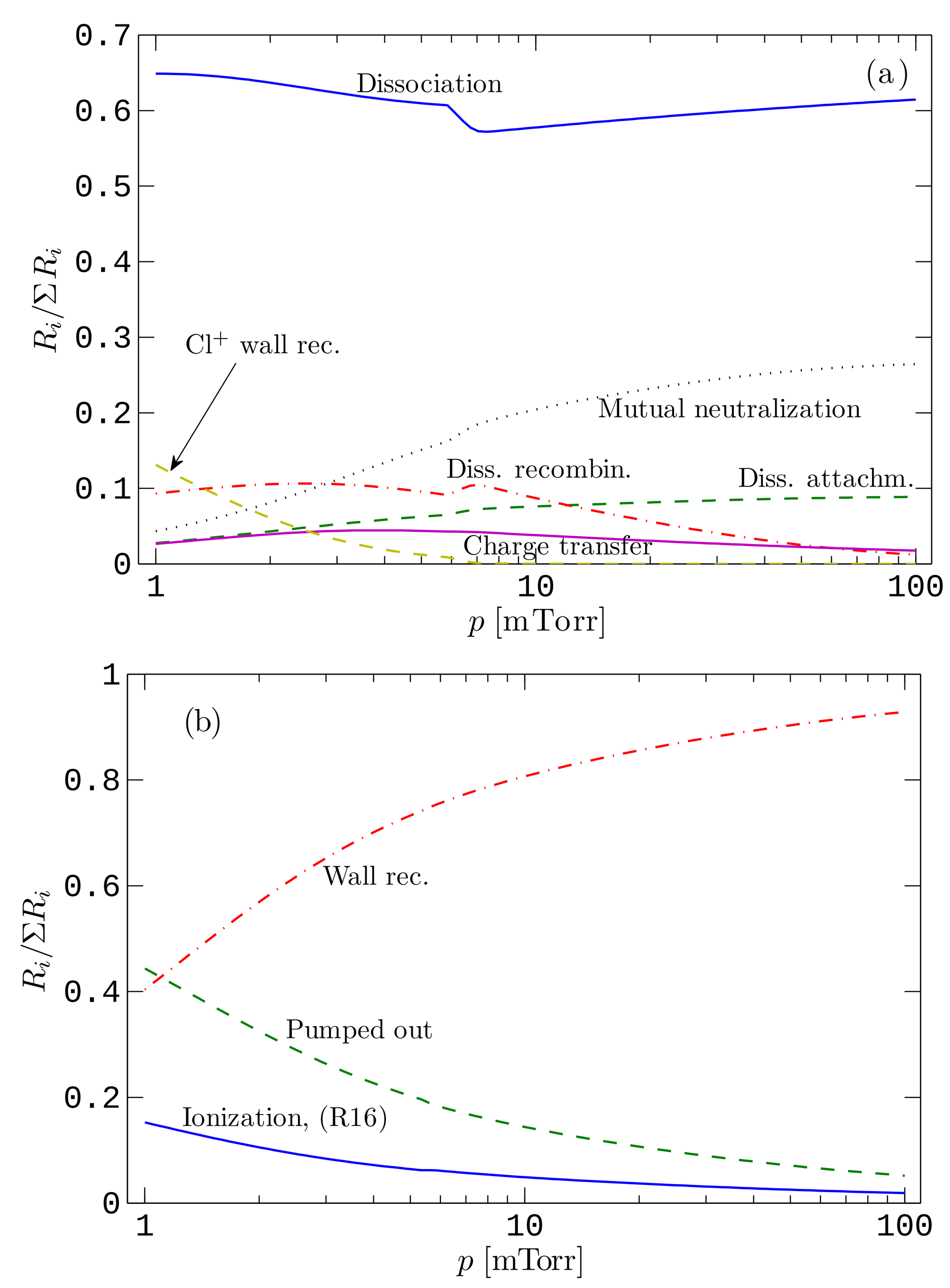

Figure 4: The relative reaction rates of (a) the creation and (b) the loss of the neutral chlorine atom Cl versus the discharge pressure at $P_{abs} = 323$ W, $Q = 100$ sccm, $R = 18.5$ cm and $L = 20$ cm.

- Electron impact dissociation is the most important channel for Cl production, wall recombination of Cl^+ is important at low pressure, and the contribution of dissociative electron attachment and mutual neutralization of Cl_2^+ and Cl^- increases with pressure
- Recombination at the wall accounts for 40 – 93 % of Cl loss and is the most important channel for Cl atom loss

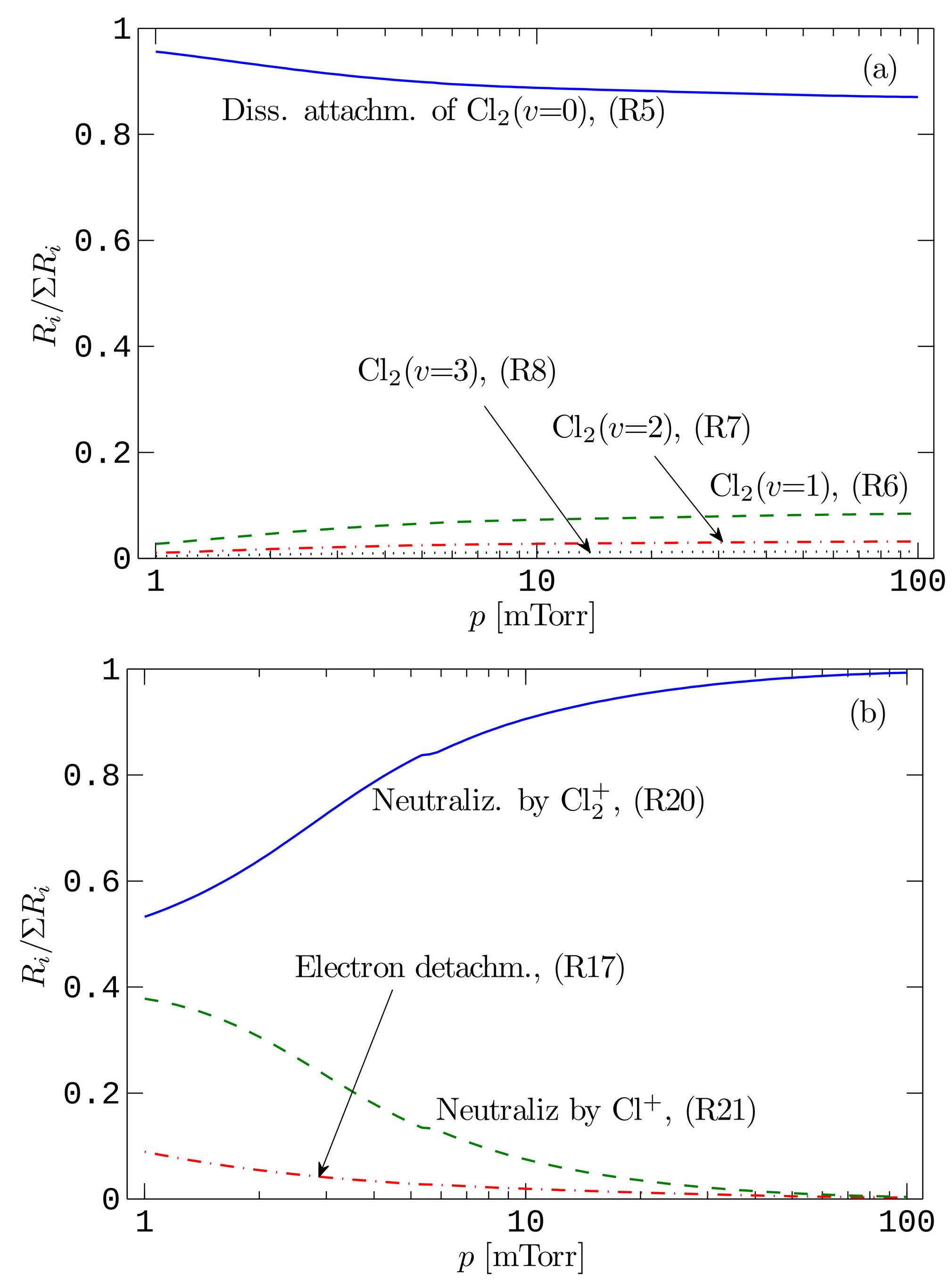

Figure 5: The relative reaction rates of (a) the creation and (b) the loss of the negatively charged chlorine ion Cl^- versus the discharge pressure at $P_{abs} = 323$ W, $Q = 100$ sccm, $R = 18.5$ cm and $L = 20$ cm.

- Production mechanism for Cl^- is inherently simple, consisting only of dissociative electron attachment to Cl_2 in different vibrational states.
- Mutual neutralization with Cl_2^+ is the most important loss process for Cl^-, especially at 100 mTorr where it is the dominating process.
- Mutual neutralization with Cl^+ is significant at low pressures, accounting for 36 % of the total loss at 1 mTorr. The electron detachment from Cl has at most 9 % contribution to the overall loss of Cl^- at 1 mTorr, but is negligible at pressures above 10 mTorr.

Conclusions

- Although the dissociation fraction decreases with decreasing power and increasing pressure, the chlorine discharge remains highly dissociated in all conditions, being over 20 % at the lowest power and highest pressure explored.
- Electron impact dissociation is responsible for most of the Cl production, or roughly 55 – 65 %. There are also several processes that contribute significantly, such as wall recombination of Cl^+, mutual neutralization and dissociative recombination of Cl_2^+.
- Cl atoms are lost mainly at the wall and to pumping.
- Cl^- ions are essentially entirely produced in dissociative attachment of electrons to Cl_2 and lost to mutual neutralization with Cl^+ and Cl_2^+.
- The electronegativity increases rapidly with decreasing dissociation fraction, i.e. increases with increasing pressure and decreasing power.
- The effect of vibrationally excited chlorine molecules $Cl_2(v > 0)$ is not great, at most increasing the Cl^- production by about 14 %.

Acknowledgments

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