Notes on the electron excitation rate coefficients for argon and oxygen discharge

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Abstract

The rate coefficients for electron impact excitation, electron impact ionization and elastic scattering of electrons for argon, oxygen atom and oxygen molecule are reviewed. We assume the electron energy distribution to be Maxwellian and the fit to the rate coefficient is valid in the range 1 – 7 eV. The rate coefficients are then used to evaluate to collisional energy loss per electron ion pair created.

1 Introduction

To describe discharge operation a noble gas such as argon is usually used [Lieberman and Lichtenberg, 1994]. However, most process gases are molecular and electronegative. The volume averaged global model for low pressure high density discharges was developed by Lieberman and Gottscho [Lieberman and Gottscho, 1994] for noble gases and extended to molecular gases by Lee et al. [Lee et al., 1994, 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]. 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].

An important quantity used in the global model is the collisional energy loss per electron-ion pair created, $\mathcal{E}_{\mathrm{c}}(T_{\mathrm{e}})$ is defined as

$$\mathcal{E}_{\mathrm{c}} = \mathcal{E}_{\mathrm{iz}} + \sum_{\mathrm{i}} \mathcal{E}_{\mathrm{ex},i} \frac{k_{\mathrm{ex},i}}{k_{\mathrm{iz}}} + \frac{k_{\mathrm{el}}}{k_{\mathrm{iz}}} \frac{3m_{\mathrm{e}}}{m_{\mathrm{i}}} T_{\mathrm{e}} \tag{1}$$

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

The main purpose of this work is to review the rate coefficients that are needed to evaluate to collisional energy loss per electron ion pair created for argon, oxygen atom and oxygen molecule.

2 Rate coefficient

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

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

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

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

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 for the velocity and kinetic energy of a particle

$$\mathcal{E} = \frac{m_\mathrm{e} v^2}{2e} \tag{4}$$

we find

$$f(\mathcal{E}) = \frac{2}{\sqrt{\pi}} \frac{1}{T_\mathrm{e}^{3/2}} \exp\left(-\frac{\mathcal{E}}{T_\mathrm{e}}\right) \tag{5}$$

to be the normalized Maxwellian electron energy distribution. Thus

$$k = \int_0^\infty \sigma(\mathcal{E}) \left(\frac{8 e T_\mathrm{e}}{\pi m_\mathrm{e}}\right)^{1/2} \frac{\mathcal{E}}{T_\mathrm{e}} \exp\left(-\frac{\mathcal{E}}{T_\mathrm{e}}\right) \frac{d\mathcal{E}}{T_\mathrm{e}} \tag{6}$$

is the rate coefficient.

3 Argon atom

Argon is a simple noble gas and is most often used as a reference for describing discharge operation. The most important rate coefficients for electron collisions in argon are electron-neutral ionization k_iz, electron impact excitation k_ex, and elastic scattering k_el. The ion-neutral collisional cross section is mainly due to resonant charge transfer of Ar^+ on Ar and elastic scattering is [Lieberman and Lichtenberg, 1994, pg. 80]

$$\sigma_\mathrm{i} \approx 10^{-18} \quad \mathrm{m}^2$$

3.1 Excitation rate coefficient

The excitation rate coefficients for the argon atom where calculated using the excitation cross sections given by Tachibana [Tachibana, 1986] for the $4s$ excited states and by Eggarter [Eggarter, 1975] for the $4p$ excited states and

Table 1: Rate coefficients for electron impact excitation of the argon atom.

Final state	Thresh. [V]	Rate coefficient [m^3/s]	Ref.
$^3P_2$	11.5	$k_{(^3P_2)} = 5.02 \times 10^{-15} \exp(-12.64/T_e)$	[Tachibana, 1986]
$^3P_1$	11.6	$k_{(^3P_1)} = 1.91 \times 10^{-15} \exp(-12.60/T_e)$	[Tachibana, 1986]
$^3P_0$	11.7	$k_{(^3P_0)} = 1.35 \times 10^{-15} \exp(-12.42/T_e)$	[Tachibana, 1986]
$^1P_1$	11.8	$k_{(^1P_1)} = 2.72 \times 10^{-16} \exp(-12.14/T_e)$	[Tachibana, 1986]
$4p$	13.2	$k_{4p} = 2.12 \times 10^{-14} \exp(-13.13/T_e)$	[Eggarter, 1975]
$4s, 4s'$	11.8	$k_{I} = 1.45 \times 10^{-14} \exp(-12.96/T_e)$	[Eggarter, 1975]
$5s, 3\bar{d}, 5s', 3d'$	14.2	$k_{II} = 1.22 \times 10^{-14} \exp(-17.80/T_e)$	[Eggarter, 1975]
$4d, 6s, 4\bar{d}, 4d'$	15.0	$k_{III} = 7.98 \times 10^{-15} \exp(-19.05/T_e)$	[Eggarter, 1975]
$6s', 5d, 7s, 5\bar{d}$			
Higher states	15.5	$k_{IV} = 8.29 \times 10^{-15} \exp(-18.14/T_e)$	[Eggarter, 1975]

three groups, II - IV, that represent all the other excited states. The rate coefficients for the excited states are listed in table 1.

The rate coefficients listed in table 1 are those used in model calculation for argon discharge where the electron energy distribution is assumed to be Maxwellian [Gudmundsson, 1996, Gudmundsson and Lieberman, 1998a].

If more accuracy is desired in calculating the excitation rate coefficients the collection assembled by Hayashi [Hayashi] has excitation cross section for 25 excited states of argon.

3.2 Ionization rate coefficient

The ionization energy for argon is $\mathcal{E}_{\rm iz} = 15.76$ V. To calculate the ionization rate coefficient the ionization cross section measured by Straub et al. [Straub et al., 1995] is used. They report $\pm 3.5\%$ absolute uncertainty. A fit to the Straub et al. data in the range 1 - 7 eV using the code written by Philip [Philip, 1998] gives

$$k_{\rm iz} = 2.34 \times 10^{-14} T_{\rm e}^{0.59} \exp(-17.44/T_{\rm e})$$

and in the range 1 - 10 eV

$$k_{\rm iz} = 2.9 \times 10^{-14} T_{\rm e}^{0.50} \exp(-17.8/T_{\rm e})$$

but the fit used before [Gudmundsson, 1996, Gudmundsson and Lieberman, 1998a] was

$$k_{\rm iz} = 7.93 \times 10^{-14} \exp(-18.9/T_{\rm e});$$

In the first global model calculation [Lee and Lieberman, 1995] the cross section data of Rapp and Englander-Golden [Rapp and Englander-Golden, 1965] was used to calculate the ionization rate coefficient as did Kannari et al. [Kannari et al., 1985].

3.3 Rate coefficient for elastic collision

The elastic collision cross section is found in the cross section collection assembled by Hayashi [Hayashi]. A fit to the calculated rate coefficient in the range 1 – 7 eV is

$$\ln(k_{\rm el}) = -31.3879 + 1.6090 \times \ln(T_{\rm e}) + 0.0618 \times (\ln(T_{\rm e}))^2 - 0.1171 \times (\ln(T_{\rm e}))^3$$

4 Oxygen atom

Oxygen is a simple diatomic gas that has been particularly well studied. However, even in a relatively simple oxygen discharge a number of species can be formed. Fortunately there exist a data set for oxygen including rate coefficients for many of the relevant reactions [Elíasson and Kogelshatz, 1986, Kossyi et al., 1992, Lieberman and Lichtenberg, 1994]. Due to this oxygen has been used to study electronegative molecular discharge.

The total ionic momentum transfer cross section for atomic oxygen is [Hickman et al., 1997].

$$\sigma_{\rm i} = 7.5 \times 10^{-19} \quad {\rm m}^2$$

4.1 Excitation rate coefficient

The excitation rate coefficients for atomic oxygen were calculated by integrating the excitation cross sections given in the review by Laher and Gilmore

Table 2: Rate coefficients, excited states of atomic oxygen.

Reaction	Thresh. [V]	Rate coefficient [m^3/s]
Non-Rydberg States		
e+O(^{3}P) $\longrightarrow$ O(^{1}D) + e	1.96	$k_{^1\mathrm{D}} = 4.54 \times 10^{-15} \exp(-2.36/T_\mathrm{e})$
e+O(^{3}P) $\longrightarrow$ O(^{1}S) + e	4.18	$k_{^1\mathrm{S}} = 7.86 \times 10^{-16} \exp(-4.489/T_\mathrm{e})$
e+O(^{3}P) $\longrightarrow$ O(^{3}P^o) + e	15.65	$k_{^3\mathrm{P}^o} = 2.53 \times 10^{-15} \exp(-17.34/T_\mathrm{e})$
Rydberg States		
e+O(^{3}P) $\longrightarrow$ O(^{5}S^o) + e	9.14	$k_{^5\mathrm{S}} = 9.67 \times 10^{-16} \exp(-9.97/T_\mathrm{e})$
e+O(^{3}P) $\longrightarrow$ O(^{3}S^o) + e	9.51	$k_{^3\mathrm{S}} = 3.89 \times 10^{-15} \exp(-9.75/T_\mathrm{e})$
e+O(^{3}P) $\longrightarrow$ O^{h*} + e	12.0	$k_{\mathrm{h}*} = 4.31 \times 10^{-14} \exp(-18.59/T_\mathrm{e})$

[Laher and Gilmore, 1990] over an assumed Maxwellian electron energy distribution and fit over an electron temperature range of 1 – 7 eV. The excitation energy for the non-Rydberg states and the two lowest radiative Rydberg states are given in table 2 as well as the corresponding rate coefficients. The two radiative Rydberg states listed in table 2 as well as the $^3\mathrm{P} \longrightarrow {}^3\mathrm{P}^o$ transition have negligible effect on the electron collisional losses. The rate coefficients for other excited states of atomic oxygen are given by the rate coefficient k_{h*} calculated from the total cross sections for excitation of atomic oxygen given by Laher and Gilmore [Laher and Gilmore, 1990] and subtracting the rate coefficient of all other reactions given in table 2. These excited states are assumed to have threshold energy of 12 V.

These excitation coefficients are consistent with those reported earlier [Gudmundsson and Lieberman, 1998b] but error exist in later work [Patel, 1998, Gudmundsson et al., 2000]. Here a new fit is made to the rate coefficient for the excitation e + O(^{3}P) $\longrightarrow$ O(^{1}D) + e.

4.2 Ionization rate coefficient

The ionization energy for the ionization of atomic oxygen is $\mathcal{E}_{iz} = 13.61$ V [Elíasson and Kogelshatz, 1986] and the ionization rate coefficient is

$$k_{\mathrm{iz}} = 9 \times 10^{-15} T_{\mathrm{e}}^{0.7} \exp(-13.6/T_{\mathrm{e}})$$

taken from [Lee et al., 1994] which is a fit to the rate coefficient given by Elíasson and Kogelshatz [Elíasson and Kogelshatz, 1986].

4.3 Rate coefficient for elastic collision

The rate constant for elastic collisions of electrons with atomic oxygen is calculated by integrating the elastic collision cross section over an assumed Maxwellian energy distribution. The elastic collision cross section is found by fitting data from the theoretical calculations by Thomas and Nesbet [Thomas and Nesbet, 1975] for $E < 2$ eV and from the review by Itikawa and Ichimura [Itikawa and Ichimura, 1990] for $E > 2$ eV. A fit of the calculated rate coefficient in the range 1 – 7 eV is

$$\ln(k_{\mathrm{el}}) = -30.9463 + 0.9484 \times \ln(T_{\mathrm{e}}) - 0.14158 \times (\ln(T_{\mathrm{e}}))^2 - 0.0154 \times (\ln(T_{\mathrm{e}}))^3$$

5 Molecular oxygen

Here we discuss the rate coefficients for electron impact excitation and ionization of the oxygen molecule as well as the rate coefficient for elastic collision of electrons.

5.1 Excitation rate coefficient

The excitation rate coefficients for the molecular oxygen calculated by integrating the excitation cross sections over an assumed Maxwellian electron energy distribution function and fit over an electron temperature range of 1 – 7 eV are listed in table 3. The cross sections are taken from the dataset compiled by Phelps [Phelps, Lawton and Phelps, 1978].

These rate coefficients were originally used in the elaborate model of the oxygen discharge developed by Patel [Patel, 1998] and later published in

Table 3: Rate coefficients for excitation of the oxygen molecule.

Reaction	Threshold [V]	Rate coefficient [m^3/s]
$e+O_2(r=0) \longrightarrow O_2(r>0)+e$	0.02	$k_{\rm rot} = 1.87\times10^{-17}\exp(-2.9055/T_{\rm e})$
$e+O_2(v=0) \longrightarrow O_2(v=1)+e$	0.19	$k_{v=1} = 2.8\times10^{-15}\exp(-3.72/T_{\rm e})$
$e+O_2(v=0) \longrightarrow O_2(v=2)+e$	0.38	$k_{v=2} = 1.28\times10^{-15}\exp(-3.67/T_{\rm e})$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2(a^1\Delta_g)+e$	0.977	$k_{a^1\Delta_g} = 1.37\times10^{-15}\exp(-2.14/T_{\rm e})$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2(b^1\Sigma_g^+)+e$	1.627	$k_{b^1\Sigma_g^+} = 3.24\times10^{-16}\exp(-2.218/T_{\rm e})$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2({\rm ex1})+e$	4.5	$k_{\rm ex1} = 1.13\times10^{-15}\exp(-3.94/T_{\rm e})$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2({\rm 1dis})+e$	6.0	$k_{\rm 1dis} = 6.86\times10^{-15}\exp(-6.29/T_{\rm e})$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2({\rm 2dis})+e$	8.4	$k_{\rm 2dis} = 3.49\times10^{-14}\exp(-5.92/T_{\rm e})$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2({\rm 3dis})+e$	9.97	$k_{\rm 3dis} = 1.44\times10^{-16}\exp(-17.25/T_{\rm e})$
$e+O_2(X^3\Sigma_g^-) \longrightarrow O_2({\rm ex2})+e$	14.7	$k_{\rm ex2} = 1.13\times10^{-15}\exp(-18.35/T_{\rm e})$

[Gudmundsson et al., 2000]. They are different from those used by Lee et al. [Lee et al., 1994, Lee and Lieberman, 1995] in their original global model calculation of oxygen.

5.2 Ionization rate coefficient

The ionization energy of the molecular oxygen is 12.06 eV. The rate coefficient for ionization of the oxygen molecule is

$$k_{\rm iz} = 9\times10^{-16}T_{\rm e}^2\exp(-12.6/T_{\rm e})$$

taken from [Lee et al., 1994] which is a fit to the rate coefficient given by Elíasson and Kogelshatz [Elíasson and Kogelshatz, 1986].

5.3 Rate coefficient for elastic collision

The elastic collision cross section is found in the cross section collection assembled by Phelps [Phelps]. A fit of the calculated rate coefficient in the range 1 – 7 eV is

$$\ln(k_{\rm el}) = -30.7683 + 0.3531\times\ln(T_{\rm e}) + 0.2068\times(\ln(T_{\rm e}))^2 - 0.0406\times(\ln(T_{\rm e}))^3$$

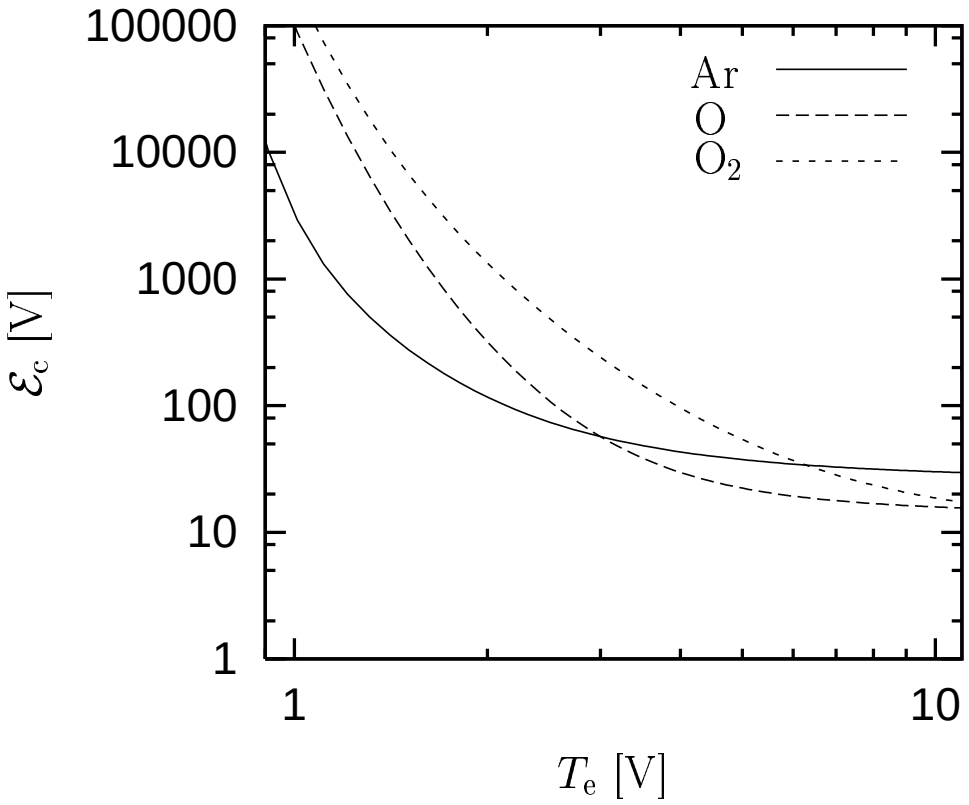

Figure 1: The collisional energy loss per electron-ion pair created $\mathcal{E}_c$ as a function of the electron temperature T_e for argon, oxygen atom and oxygen molecule.

6 Collisional loss

The collisional energy loss per electron-ion pair created $\mathcal{E}_c$ as a function of the electron temperature T_e is shown in figure 1 for argon, oxygen atom and oxygen molecule. At low electron temperature elastic transfer is the dominant contributor to the collisional energy loss. At high electron temperature the energy loss $\mathcal{E}_c$ asymptotes to somewhat higher than $\mathcal{E}_{iz}$. For molecular gases such as oxygen additional energy losses include excitation of vibrational and rotational energy levels, molecular dissociation etc. Thus in molecular gas $\mathcal{E}_c$ is significantly higher than for noble gas at a given electron temperature.

In this work the electron energy distribution is assumed to be Maxwellian and the fit to the rate coefficient is valid in the range 1 – 7 eV. The effect of the electron energy distribution on the collisional energy loss per electron-ion pair created in argon discharge is investigated elsewhere [Gudmundsson, 2001]. There the collisional energy loss is calculated while varying the electron energy distribution function from Maxwellian to Druyvesteyn distribution.

7 Conclusion

The rate coefficients used to evaluate the collisional energy loss per electron ion pair created are reviewed for argon and atomic and molecular oxygen. The electron energy distribution is assumed to be Maxwellian and the fit to the rate coefficient is valid in the range 1 – 7 eV.

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