Calculation of electron-impact excitation and ionisation cross sections and reaction rate coefficients for C, N and O atoms

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Abstract. This work concerns the calculation of electron-impact excitation and ionisation cross sections and reaction rate coefficients for carbon, nitrogen and oxygen atoms. Several analytical formulas proposed in the literature are used to calculate cross sections and rate coefficients for excitation of optically allowed and parity/spin forbidden transitions and for ionisation from electronic levels of the atoms. Theoretical calculations are then compared with each other and confronted to available experimental cross sections in order to deduce the most accurate analytic rate coefficient formula, which will be used in the implementation of Collisional-Radiative (CR) model for C-N-O-containing plasmas. The cross section and the reaction rate database created will be used in the development of a multi-temperature CR model allowing the determination of the population number densities inside an electric arc generated between two graphite electrodes and dedicated to the synthesis of carbon nanoparticles.

1. Introduction

Most of theoretical studies regarding electric arcs or thermal plasma processes and applications are achieved assuming the Local Thermodynamic Equilibrium (LTE) assumption with the development of Magneto-Hydrodynamic (MHD) models [1]. However, the LTE assumption is not effective in some particular regions of the plasma: in the vicinity of the electrodes and the walls and in the external areas of the arc where the pumping of contiguous cold gas has a significant effect. The LTE hypothesis is also unclear during arc decay or for low power arcs. In this last case, the temperature and the electron number density remain relatively low, even on the axis of the plasma. Thus, the energy transfer between the electrons and heavy particles is not efficient enough to preserve the equal distribution of energy between the various chemical species. The consequence is that the electrons have a kinetic temperature T_e higher than that of the heavy species T_h.

To study theoretically this kind of discharge, taking into account the possible occurrence of departures from thermal equilibrium, it is necessary to develop multi-T MHD models. The implementation of these multi-T models is based upon 2T thermodynamic and transport property databases and the first unavoidable step in obtaining these 2T properties is the calculation of the plasma composition. Several methods are available in the literature for the calculation of multi-T plasma compositions: the minimization of a thermodynamic function [2], the law of mass action [3] and the kinetic/collisional-radiative (CR) model [4-7]. However, it is now clearly established that the best and more accurate way to obtain the plasma composition under thermal non equilibrium conditions is the CR model. Indeed, compared to the other techniques, this kind of approach avoids the use of simplifying assumptions associated with the internal excitation modes (electronic, vibrational and rotational). On the other hand, CR models are more complex to develop because they require the availability of an extended cross sections or reaction rate coefficients database for all inelastic collisional processes between the chemical species (internal
levels) of the plasma. Moreover, the population densities obtained from CR models in non-thermal equilibrium conditions are highly dependent on the accuracy of the cross section or reaction rate databases injected in the CR model. As a consequence, it is very important to ensure that cross-sections or reaction rates used in a CR model are accurate in order to obtain exact values of population densities. We will present in this paper a comparison of experimental and theoretical cross sections and reaction rate coefficients data for C, N and O. The aim of this study is to retain the more accurate theoretical formalism allowing the computation of cross sections and rate coefficients as a function of the collisional mechanism (excitation or ionization) by comparing the various formalisms with available experimental data.

2. Theory
In this section, we will present the most widely used analytical formulas given in literature to calculate ionization and excitation rate coefficients. The rate coefficient is given assuming a Maxwellian distribution by,

$$ k_{if} = \frac{8\pi m_e}{\pi} \left( \frac{1}{K_B T} \right)^3 \int_{E_0}^{\infty} \sigma_{if}(E) \exp \left( \frac{E}{K_B T} \right) dE $$

where \( m_e \) is the electron mass, \( K_B \) is the Boltzmann constant, \( E \) is the collision energy, \( E_0 \) is the threshold energy, \( \sigma_{if}(E) \) is the cross section from state \( i \) to \( f \) in units of \( m^2 \) and \( T \) is the plasma/electronic temperature.

The main analytical formulas given in literature to calculate ionization and excitation rate coefficients are the following:

According to Annaloro et al. [8], the ionization rate coefficient \( k_i^+ \), starting from an initial electronic state \( i \), is given by,

$$ k_i^+ = \frac{8K_B T}{\pi m_e} 4\pi a_0^2 y^2 \alpha^+ \left( \frac{E_{ion}}{E_{ion} - E_i} \right)^2 \left[ \ln(1,25\beta^+) \left( y^{-1} e^{-y} - \xi_{1}(y) \right) + y^{-1} \xi_{1}(y) - G_2(y) \right] $$

Voronov [9] and Goldstein [10] propose two formulas to calculate this rate coefficient given successively by Equations 3 and 4,

$$ k_i^+ = \frac{A_{14} P}{x+y} y^k e^{-y} $$

$$ k_i^+ = 3.84 \times 10^{-6} \frac{y^{0.88}}{y^2 + 1.75y + 0.11} y e^{-y} k_B T $$

For electronic excitation transitions, we distinguish allowed, spin forbidden and parity forbidden transitions. Drawin [7] and Annaloro et al. [8] propose a rate coefficients based on the maxwellian distribution for each kind of excitation transition (Equations 5 to 7):

$$ k_{if} = \frac{8K_B T}{\pi m_e} 4\pi a_0^2 y^2 \alpha^+ \left( \frac{E_{ion}}{E_{ion} - E_i} \right)^2 \left[ \ln(1,25\beta^+) \left( y^{-1} e^{-y} - \xi_{1}(y) \right) + y^{-1} \xi_{1}(y) - G_2(a) \right] $$

for the excitation of an optically allowed transition

$$ k_{if} = \frac{8K_B T}{\pi m_e} 4\pi a_0^2 y^2 \alpha^+ \left( \frac{E_{ion}}{E_{ion} - E_i} \right)^2 \left[ \ln(1,25\beta^+) \left( y^{-1} e^{-y} - \xi_{1}(y) \right) + y^{-1} \xi_{1}(y) - G_2(a) \right] $$

for the excitation of a parity forbidden transition

$$ k_{if} = \frac{8K_B T}{\pi m_e} 4\pi a_0^2 y^2 \alpha^+ \left( \xi_{2}(y) - \xi_{4}(y) \right) $$

for the excitation of a spin forbidden transition

The rate coefficient suggested by Giannaris and Incropera [11] and Mansbach and Keck [12] are given by equations 8 and 9 respectively:

$$ k_{if} = 61.37 \frac{g_l}{g_f} A_l y^{-3} e^{-y} P(y) T^{-3.5} $$

for the excitation of an optically allowed transition
\[ k_{fi} = 9.5710^{-6} \left( \frac{\varepsilon_i}{k_B T} \right)^{2.5} \left( \frac{\varepsilon_f}{k_B T} \right)^{-4.83} \left( \frac{1}{k_B T} \right)^{1.5} \]  

(9)

for the de-excitation of a forbidden transition

Where (in equations 2 to 9) \( a_0 \) is the first Bohr radius, \( E_{ion}^H \) and \( E_{ion}^M \) the ionization energies of hydrogen and of the species M considered. \( E_i \) is the energy of the initial electronic level. \( A, P, W, k \) are fit parameters [13]. The parameters \( \alpha^{APS}, \beta^{APS} \) are chosen as mean values resulting from comparisons with experimental cross sections [14]. \( g_i \) and \( g_f \) are the degeneracies of the electronic levels, \( \alpha_{fi} \) is the Einstein coefficient. \( \varepsilon_i = (E_{ion}^M - E_i) \), \( \varepsilon_f = (E_{ion}^M - E_f) \) and \( y = (E_{ion}^M - E_i)/k_B T \). \( \xi_p(y) \) and \( G_p(y) \) are the exponential integral and the generalized integral of the order \( p \) (equations 10 and 11).

\[ \xi_p(y) = \int_1^{\infty} e^{-yx} x^p dx \]  

(10)

\[ G_p(y) = \frac{1}{(p-1)!} \int_1^{\infty} e^{-yx} [\ln(x)]^{p-1} dx \]  

(11)

3. Electron-impact excitation and ionization cross sections

The cross sections presented and compared in this work are taken from various databases such as, LXCAT [15], NIST [16], NIFS [17], and from previous experimental works and numerical (or theoretical) calculations. Different models have been employed to calculate cross section of atoms and molecules by electron impact collision such as: the R-matrix with pseudo-states (BSR) [18-21], the Binary-Encounter-Bethe (BEB) model [22] and the convergent close-coupling (CCC) theory [23]. On the other hand there are various experimental methods implemented for cross section measurements such as, the crossed beams in which fast beams of atoms are produced by charge capture of 2 to 4 keV ions in a gas target [24] and the apparatus method with modulated crossed-beams type with three differentially-pumped vacuum chambers to isolate the source and detector regions used by Williams et al. [25-27].

Figure 1. Ionization cross section for carbon from fundamental state as a function of electron energy. The BSR-696 calculation of Wang et al. [28] are compared with the BEB predictions of Kim and Desclaux [29], the calculations of Bell et al. [30] and the experimental data of Brook et al. [24]. T: theoretical, E: experimental.
Many numerical and theoretical cross section calculations for atomic species were previously studied but only few experimental measurements exist. Indeed, to our knowledge there are no available experimental cross section measurements for carbon except for ionization. However, for nitrogen and oxygen the comparison between numerical and experimental data is achievable because experimental data for excitation and ionization are available. The various transitions treated in the present work are presented in table 1.

Electron impact ionization cross sections of carbon are presented in figure 1 as a function of electron energy. As we know that inelastic collision processes such as excitation or ionization are important to study the chemical kinetic of thermal plasma it is very important to determine accurately the cross section or reaction rate coefficients for these collision processes. The main criteria to highlight the best numerical cross section that better fit experimental measurements are (a) the threshold position of the reaction process which is equal to the energy difference between the two states considered, (b) the position of the cross section maximum which gives the optimal value of the reaction and the electronic energy involved, (c) the behavior of the cross section on the whole electronic energy range. So based on those criteria, we can deduce that the calculation of Wang et al. [28] and Bell et al. [30] fitted well experimental measurements for carbon as shown in figure 1.

For excitation processes we have studied several cases for both allowed transitions and forbidden transitions. Two transitions are presented in figures 2 and 3 for both oxygen and nitrogen allowed and forbidden transitions successively. For the first transition of oxygen (figure 2) we see clearly the good agreement between experimental and theoretical cross sections of Johnson et al. [34, 35].

As we mentioned in the abstract, the aim of this work is to deduce an analytical formula to calculate rate coefficients which best fit experimental measurements. So in the next section we will integrate our recommended previous cross sections using the Maxwell distribution for a temperature range from 4 kK to 20 kK. The obtained reference reaction rate will be confronted with values issued from available analytical formulas.
Figure 3. Excitation cross section for the parity forbidden transition of nitrogen from fundamental state to the \(2s^22p^3\) \(^1\)D state as a function of electron energy. The BSR-690 calculation of Wang et al. [31] are compared with the calculations of Berrington et al. [37] and the experimental data of Ormonde et al. [38].

For the second transition in nitrogen (figure 3), the data of Wang et al [31] are in good agreement with experimental values of Ormonde et al [38].

Table 1. Electronic levels of this work [16]. I: ionization, PF: parity forbidden, A: allowed and SF: spin forbidden

| Species | Lower | Upper | Energy (eV) | Recommended formalism |
|---------|-------|-------|-------------|-----------------------|
| Carbon  | \(2s^2\) \(2p\)^2 \(^3\)P | \(C'(2s^2\) \(2p\)^2 \(^3\)P) | 11.26\(^\dagger\) | Voronov [9] |
|         | \(2p^2\) \(^1\)D | 1.26\(^\text{PF}\) | Mansbach et Keck [12] |
|         | \(2s^2\) \(2p\)^2 \(^1\)S | 2.68\(^\text{PF}\) | Mansbach et Keck [12] |
|         | \(2s^2\) \(2p\)^3 \(^3\)P | 7.48\(^\text{A}\) | Drawin [7,8] |
|         | \(2s^2\) \(2p\)^3 \(^3\)P | 9.33\(^\text{A}\) | Drawin [7,8] |
|         | \(2s^2\) \(2p\)^3 \(^3\)D | 9.70\(^\text{A}\) | Giannaris [11] |
|         | \(2s^2\) \(2p\)^3 \(^3\)P | 9.83\(^\text{A}\) | Giannaris [11] |
| Nitrogen | \(2s^2\) \(2p\)^3 \(^4\)S | \(N'(2s^2\) \(2p\)^2 \(^3\)P) | 14.53\(^\dagger\) | Voronov [9] |
|         | \(2s^2\) \(2p\)^3 \(^3\)D | 2.38\(^\text{PF}\) | Mansbach et Keck [12] |
|         | \(2s^2\) \(2p\)^3 \(^3\)P | 3.57\(^\text{SF}\) | Mansbach et Keck [12] |
|         | \(2s^2\) \(2p\)^3 \(^3\)P | 10.32\(^\text{A}\) | Drawin [7,8] |
|         | \(2s^2\) \(2p\)^3 \(^4\)P | 10.92\(^\text{A}\) | Drawin [7,8] |
|         | \(2s^2\) \(2p\)^3 \(^4\)P | 12.84\(^\text{A}\) | Drawin [7,8] |
|         | \(2s^2\) \(2p\)^3 \(^4\)P | 12.99\(^\text{A}\) | Drawin [7,8] |
| Oxygen  | \(2s^2\) \(2p\)^4 \(^1\)P | \(O'(2s^2\) \(2p\)^2 \(^4\)S) | 13.61\(^\dagger\) | Voronov [9] |
|         | \(2s^2\)^2 \(2p\)^3 \(^1\)D | 1.96\(^\text{PF}\) | Drawin [7,8] |
|         | \(2s^2\) \(2p\)^3 \(^1\)S | 4.18\(^\text{SF}\) | Mansbach et Keck [12] |
|         | \(2s^2\) \(2p\)^3 \(^3\)S | 9.52\(^\text{A}\) | Drawin [7,8] |
|         | \(2s^2\) \(2p\)^3 \(^3\)P | 10.98\(^\text{A}\) | Drawin [7,8] |
|         | \(2s^2\) \(2p\)^3 \(^3\)D | 12.08\(^\text{A}\) | Drawin [7,8] |
|         | \(2s^2\) \(2p\)^3 \(^3\)D | 12.53\(^\text{A}\) | Drawin [7,8] |
4. Results and Discussion

In this work, our focus has been on rate coefficients of inelastic processes which are indispensable in the implementation of multi-T CR models that allows to access the population number densities of chemical species. Under non-thermal equilibrium conditions, it is important to understand the effect of the rate coefficients used in the CR model and their impact on species densities. On the other hand, for some processes there are no available cross section data allowing the calculation of the rate coefficients. As a consequence, it is important to recommend analytical formulas for each transition taken into account in the plasma modelling.

Ionization rate coefficients of carbon are displayed in figure 4 as a function of electron temperature. The rate coefficients of Bell et al. [30] and Wang et al [28] (BSR-696) are very close to the analytical formulas of Voronov [9] contrarily to those of Drawin [7] and Goldstein [10]. For nitrogen and oxygen, the conclusions are the same for ionization. The formalism of Voronov exhibits the best agreement with the experimental rate coefficient. These conclusions are reported in the last column of table 1. Figure 5 shows the rate coefficients for the allowed transition $2p^4 \, ^3P \rightarrow 3s \, ^3S$ in oxygen. The analytical formulas of Drawin [8] and Giannaris and Incropera [11] are relatively far from the rate of Johnson et al. [35] with a smaller gap for Drawin’s formula. Other allowed transitions and our conclusions concerning the choice of the best formalism are displayed in table 1. An example of parity forbidden transition for nitrogen is displayed in figure 6. The analytical formula of Mansbach and Keck [12] fit well the correspondent rate coefficient of BSR-690 [31].

As a conclusion, the analytical formula of Drawin is more efficient in case of allowed transitions, and the one of Mansbach et Keck [12] is recommended for forbidden transitions (cf. table 1).
Figure 5. Excitation rate coefficient for an optically allowed transition of oxygen from fundamental state to the \(2s^22p^1(^4S)\) \(3s\ \!(^3S)\) state as a function of electron temperature. T: theoretical; AF: analytical formula.

Figure 6. Excitation rate coefficient for an parity forbidden transition of nitrogen from fundamental state to the \(2s^22p^3(^2D)\) state as a function of electron temperature. T: theoretical; AF: analytical formula.

5. Conclusion
Our aim in this paper was to study the electron-impact excitation and ionisation cross sections and reaction rate coefficients for C, N and O atoms, which are essential in the implementation of multi-T CR models. The comparison of ionization rate coefficients calculated from experimental cross sections with
those obtained from analytical formulas show that the formalism of Voronov [9] exhibits the best agreement. For electron-impact excitation, as mentioned in table 1, the analytical formulas are depending of the transitions types and the considered atom. However, as a general conclusion we can say that the Drawin [7] formula is more efficient in the case of allowed transitions, whereas Mansbach and Keck [12] is recommended for forbidden transitions.

In a forthcoming work we will introduce the chosen analytical formulas in a 2-T CR model for C-N-Ar-He-Ni-Co-containing plasmas in order to obtain population number densities for arc discharges dedicated to the synthesis of carbon nanotubes.

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References
[1] A. Gleizes, J. J. Gonzalez, and P. Freton, J. Phys. D: App. Phys. 38, R153 (2005)
[2] R. A. Aliberti, J. Pure and Applied Chem. 73, 1349 (2001)
[3] D. Godin and J. Y. Trépanier, Plasma Chem. and Plasma Proc. 24, 3, 447-473 (2004)
[4] J. Bacri, A. Médani, Physica C 101, 3, 399-409 (1980)
[5] J. Bacri, M. Lagréca, and A. Médani, Physica C 113, 3, 403-418 (1982)
[6] H. W. Drawin and P. Felenbok, Data for plasma in LTE, Ed. Gauthier-Villars, Paris (1965)
[7] H. W. Drawin and F. Emard, Zeitschrift für Physik A 254, 3, 202-217 (1972)
[8] J. Annaloro, P. Teulet, A. Bultel, Y. Cressault, and A. Gleizes, Eur. Phys. J. D 71, 12 (2018)
[9] G. S. Vornovo, Atomic Data and Nuclear Data Tables 65, 1, 1-35 (1997)
[10] R. Goldstein, Jet Propulsion Laboratory. Pasadena, CA, USA: NASA Tech Report, (1969)
[11] R. J. Giannaris and F. P. Incropera, J. Quan. Spec. and Rad. Transfert. 3, 291-307 (1971)
[12] P. Mansbach and J. Keck, Phys Rev 181, 1, 275-289 (1969)
[13] V. Regemorter, American Astronomical Society, 3, 906-915 (1962)
[14] A. Bultel, B. V. Ootegem, A. Bourdon, P. Vervisch, Phys. Rev. E 65, 4 (2002)
[15] LXCat DataBase, http://www.lxcat.laplace.univ-tlse.fr
[16] NIST DataBase, https://www.nist.gov/
[17] NIFS DataBase, https://dbshino.nifs.ac.jp/
[18] O. Zatsarinny and S. S. Tayal, J. Phys. B: At. Mol. Opt. Phys. 34, 7, 23 1299-1319 (2001)
[19] O. Zatsarinny and S. S. Tayal, J. Phys. B: At. Mol. Opt. Phys. 34, 17, 3383-3400 (2001)
[20] O. Zatsarinny and K. Bartschat, J. Phys. B: At. Mol. Opt. Phys. 37, 10, 2173-2189 (2004)
[21] O. Zatsarinny and K. Bartschat, J. Phys. B: At. Mol. Opt. Phys. 37, 23, 4693-4706 (2004)
[22] Y. K. Kim and M. E. Rudd, Phys. Rev. A 50, 5, 3954-3967 (1994)
[23] I. Bra, Phys. Rev. A 49 1066–82 (1994)
[24] E. Brook, M. F. A. Harrison, and A. C. H. Smith, J. Phys. B 11, 17, 3115-3132 (1978)
[25] J. F. Williams and B. A. Willis, J. Phys. B: At. Mol. Phys. 8, 10, 1641-1669 (1975)
[26] J. F. Williams, J. Phys. B: At. Mol. Opt. Phys. 21, 11, 2107-2116 (1988)
[27] J. F. Williams and L. J. Allen J. Phys. B: At. Mol. Opt. Phys. 22, 21, 3529-3539 (1989)
[28] Y. Wang, O. Zatsarinny, and K. Bartschat, Phys. Rev. A 87, 012704 (2013)
[29] Y. K. Kim and J. P. Desclaux, Phys. Rev. A 66, 012708 (2002)
[30] K. L. Bell et al. J. Phys Chem. Rev. Data 12, 4, 891-916 (1983)
[31] Y. Wang, O. Zatsarinny and K. Bartschat, Phys. Rev. A 89, 062714 (2014)
[32] S. S. Tayal, and Oleg Zatsarinny, Phys. Rev. A 94, 042707 (2016)
[33] S. S. Tayal, J. Geophys. Research. 109, A08301 (2004)
[34] P. V. Johnson et al. J. Phys. B: At. Mol. Opt. Phys. 36, 21, 4289-4299 (2003)
[35] P. V. Johnson, J. W. McConkey, S. S. Tayal, and I. Kanik, Can. J. Phys. 83, 6, 589-616 (2005)
[36] S. O. Vaughan and J. P. Doering, J. Geophys. Research. 92, 7749 (1987)
[37] K. A. Berrington, P. G. Burke, and W.D. Robb, J. Phy B 8, 15, 2500-2511 (1975)
[38] S. Ormonde, K. Smith, B. W. Torres and A. R. Davies, Phys. Rev. A 8, 262-295 (1973)