

# Electron and Vibrational Kinetics in Supersonic Nozzle Expansion

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**Abstract.** Vibrational and electron kinetics, as well as electronic excited states and ionization kinetics, have been coupled self consistently solving master and Boltzmann equation at the same time. These kinetics have been inserted in a quasi one-dimensional code for the high enthalpy nozzle expansion.

## INTRODUCTION

The supersonic expansion through a nozzle flow is characterised by strong non-equilibrium conditions. Multitemperature approach does not describe correctly the vibrational distributions. In previous works [1-3] we have shown the non-Boltzmann character of the vibrational distributions in  $N_2/N$  [1], and air mixtures [2,3], especially when atom recombination is dominant; starting with very high temperature in the reservoir, the gas is partially dissociated and during the expansion the recombination is strong, generating non-Boltzmann vibrational distributions. As a consequence, the global dissociation rates do not follow the Arrhenius dependence on the local temperature.

If the reservoir temperature is high enough to have ionization degree of the order of  $10^{-3} \div 10^{-1}$ , electron-molecule (e-M) collisions cannot be neglected. The conditions of the system during the supersonic expansion can be compared to post-discharge [4]: energy trapped in internal degrees of freedom (vibrational and electronic excited states) and electron kinetic energy are very high. therefore the system should relax to reach the equilibrium with the translational temperature of molecules. In the nozzle supersonic expansions there is a further difficulty due to the fact that gas temperature and pressure change during the expansion, while these quantities are constant in post-discharge systems.

Even if ionization degree is high, electron-electron collisions, though very important, are not sufficient to overcome the effect of superelastic and inelastic collisions, and therefore non-Maxwell electron energy distributions are obtained [4]. To model non-equilibrium vibrational distributions in presence of non maxwellian electron energy distributions it is necessary to solve contemporary the master equations for the vibrational kinetics and the Boltzmann equation for free electrons (self-consistent model).

The self-consistent model has been applied in flow conditions for the boundary layers of hypersonic re-entering body [5] and for nozzle supersonic expansion [6], neglecting ionization and electronically excited state kinetics, showing strong effect of the self-consistent coupling in both vibrational and electron energy distribution functions (eedf); electronically excited states fraction as well as ionization degree have been considered constant. In recent work [7] we have applied the model to the conic nozzle adding the electronically excited states and ionization/recombination kinetics. The results have shown that as supposed in previous works ionization degree is practically constant, because the pressure is

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**14. ABSTRACT**  
Vibrational and electron kinetics, as well as electronic excited states and ionization kinetics, have been coupled self consistently solving master and Boltzmann equation at the same time. These kinetics have been inserted in a quasi one-dimensional code for the high enthalpy nozzle expansion.

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very low, but electronically excited states change in a range of many orders of magnitude. Strong non-equilibrium distributions are obtained, with a strong effect of superelastic collisions.

In this work we have applied the model used in [7] to F4 nozzle [8] to study the effect of a different nozzle profile.

## NUMERICAL MODEL

The model used to calculate the nozzle fluid dynamics is based on the quasi one-dimensional steady Euler equations [1-3]

$$\left\{ \begin{array}{l} \frac{d\rho u A}{dx} = 0 \\ \frac{dP}{dx} + \rho u \frac{du}{dx} = 0 \\ u \frac{du}{dx} + \frac{dh}{dx} = 0 \\ \frac{d\rho_{sv} u A}{dx} = S_{sv}^0 \\ P = \frac{\rho R T}{m} \end{array} \right. \quad (1)$$

for reacting flows, where " $\rho_{sv}$ " is the mass density of the species  $s$  in level  $v$ . These equations are completed by the definition of the enthalpy for a non-equilibrium flows

$$h = h_T + h_i + h_e \quad (2)$$

as the sum of the translational (eq. 3), internal (eq. 4) and free electron (eq. 5) enthalpy

$$h_T = RT \frac{\sum \alpha_s \chi_s}{\sum m_s \chi_s} = \frac{\alpha RT}{m} \quad (3)$$

$$h_i = \frac{1}{m} \left[ \sum_s \chi_s (H_s^f + f_{sv} \epsilon_{sv}) \right] \quad (4)$$

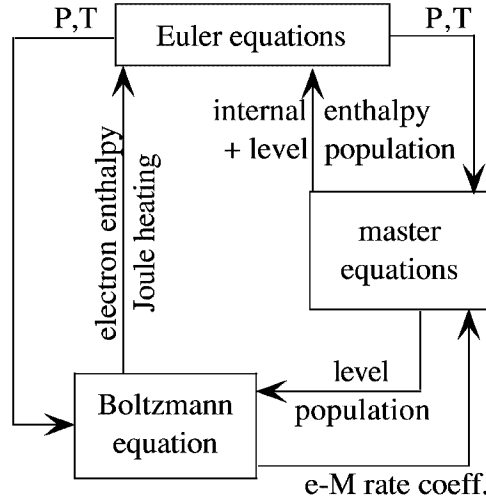
$$h_e = \frac{1}{m} \left[ RT + \int \epsilon n(\epsilon) d\epsilon \right] \quad (5)$$

The quantity " $f_{sv}$ " is the energy level distribution or the fraction of heavy particle of  $s$ -th species in the  $v$ -th level and " $n(\epsilon)$ " is the eedf.

The contribution of reactions is included in the mass continuity equation for any single species (see eq. 1) where the source term can be calculated from the zero-dimensional kinetic equations obtaining the following expression for species mass fraction

$$\frac{dc_{sv}}{dx} = \frac{S_{sv}^o}{\rho u A} = \frac{m_s S_{sv}^n}{\rho u A} \quad (6)$$

This model has been applied to study vibrational and chemical kinetics and can be easily extended to the electronically excited states. Some rearrangements are needed to extend the nozzle model when electron kinetics is coupled self-consistently with vibrational and excited level (vibrational and electronic) kinetics (see fig. 1).

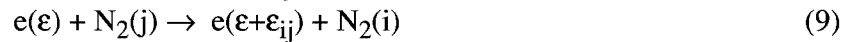


**FIGURE 1.** Scheme of the self-consistent coupling between, heavy particle, electron kinetics and Euler equations.

As starting point we consider the Boltzmann equation for free electrons in the homogeneous and almost isotropic (two terms in spherical harmonics expansion) approximation [9]. The time dependent eedf can be calculated solving the equation

$$\frac{\partial n(\epsilon)}{\partial t} = -\frac{\partial}{\partial \epsilon} (J_E + J_{el} + J_{ee}) + S_{in} + S_{sup} \quad (7)$$

where  $J_E$ ,  $J_{el}$ ,  $J_{ee}$  are the flux along the electron energy axis due respectively to electric field (E), electron-heavy particle (el) and electron-electron elastic collisions and  $S_{in}$  and  $S_{sup}$  are the source terms due to inelastic (eq. 8) and superelastic (eq. 9) collisions ( $i < j$ ).

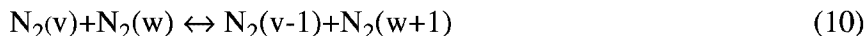


The "J" terms depend on the derivatives (first and second) of the eedf while "S" terms make the electron to jump from one energy to another and are proportional to the eedf. All the terms are linear but " $J_{ee}$ " which is quadratic in the eedf [11].

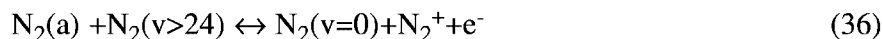
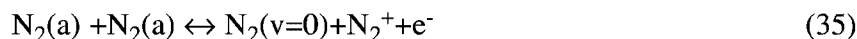
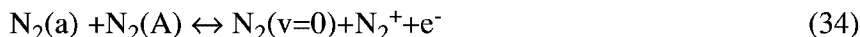
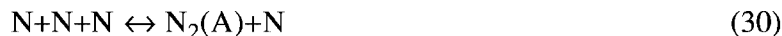
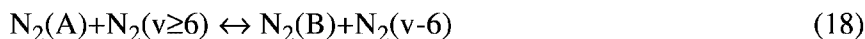
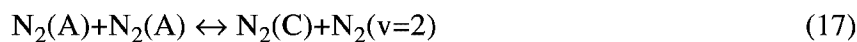
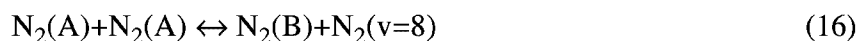
The numerical approach to the solution of the nozzle equations has been widely described in previous works [1-3,7]. For  $N_2$  gas, the species considered are  $N_2$ ,  $N_2^+$ ,  $N$ ,  $N^+$ ,  $e^-$ . Only for nitrogen

molecules, internal level kinetics has been taken into account, considering 45 vibrational levels and four electronically excited states  $A^3\Sigma_u(N_2(A))$ ,  $B^3\Pi_g(N_2(B))$ ,  $C^3\Pi_g(N_2(C))$  and  $a^1\Sigma_u^-(N_2(a))$ .

We have used the same vibrational and dissociation/recombination kinetics used in [1-3]



To this model we have added electronically excited states and ionization/recombination kinetics [7]



These processes are considered mainly in cold discharge models and the data are quite scanty [11-17]. In general, for those processes for which the analytical dependence of the rate coefficient on the temperature is unknown, the exothermic rate has been considered constant and the rate of the reverse process is calculated applying the detailed balance principle [1-3] which assures the existence of the equilibrium state.

This reaction scheme has been improved by adding electron-molecule collision processes, in particular vibrational and electronic inelastic (eq. 8) and superelastic (eq. 9) collisions. The rate coefficients of these processes are calculated from the eedf

$$R_{vw} = \int_0^{\infty} n(\epsilon) \sigma_{vw}(\epsilon) v(\epsilon) d\epsilon \quad (37)$$

The same can be written for reactive e-M processes such as dissociation and ionization. The cross sections ( $\sigma$ ) of e-M processes can be found in [19-26]. It should be noted that in the present paper recombination of atomic nitrogen pumps either the ground state through the ladder climbing model or the electronically excited states through reactions 27-30.

## RESULTS AND DISCUSSION

The model previously described has been applied to the F4 nozzle [2] (see fig. 2).

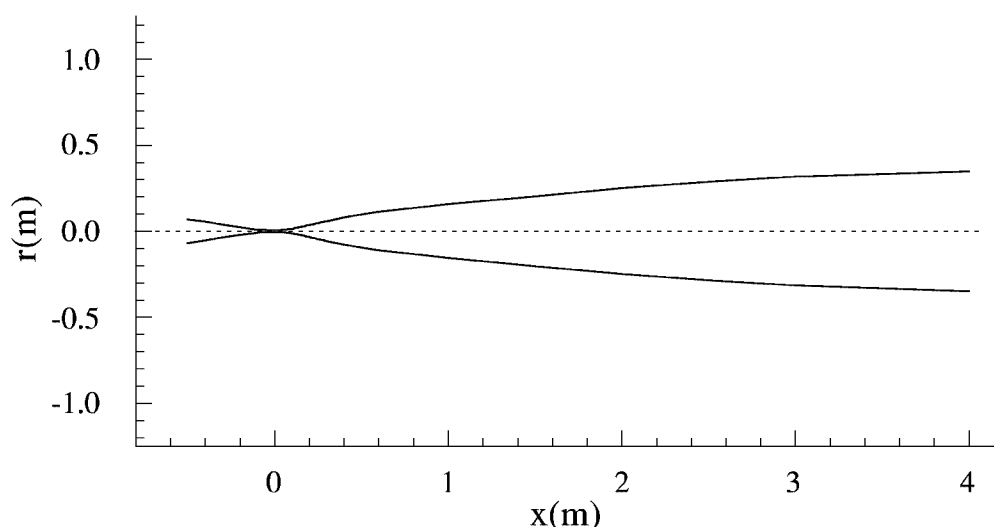


FIGURE 2. F4 nozzle section.

In this paper we investigate the role of electronically excited states and free electron kinetics on the F4 nozzle flow. At this purpose we have compared the results obtained with three different kinetic models;

- (a) = only vibrational and vibrational-dissociation kinetics (proc. 10÷15),
- (b) = (a) + electronically excited state kinetics (proc 10÷36),
- (c) = (b) + free electron kinetics (proc 8÷36).

To study the role of electron kinetics on the state-to-state kinetics, we have chosen as stagnation conditions  $T_0 = 10000$  K and  $P_0 = 1$  atm. In previous works [5,6], the ionization kinetics have been neglected, supposing constant electron molar fraction. In reference [7], where the self-consistent model includes ionization/recombination kinetics for the conic nozzle, we have shown that electron density is practically constant. The same results has been obtain in this work. On the contrary, electronically excited states kinetics [7] seems to have strong effects also on macroscopic quantities, as can be observed in fig. 3 where the mach number calculated in the three cases a, b, c has been compared.

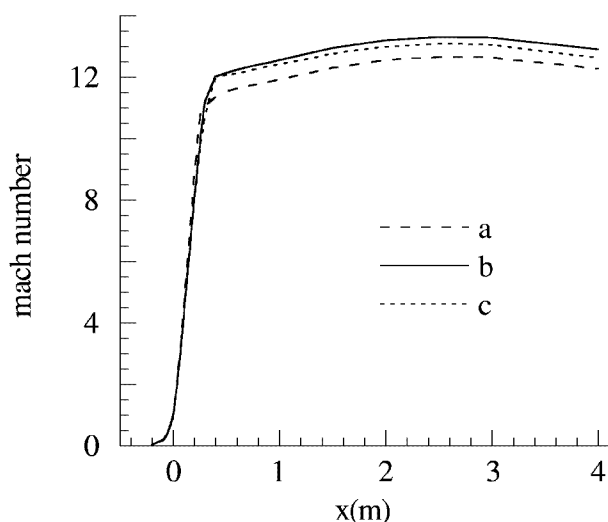


FIGURE 3. Mach number profile calculated in different kinetic models; a proc 10-15, b proc 10-36, c proc 8-36.

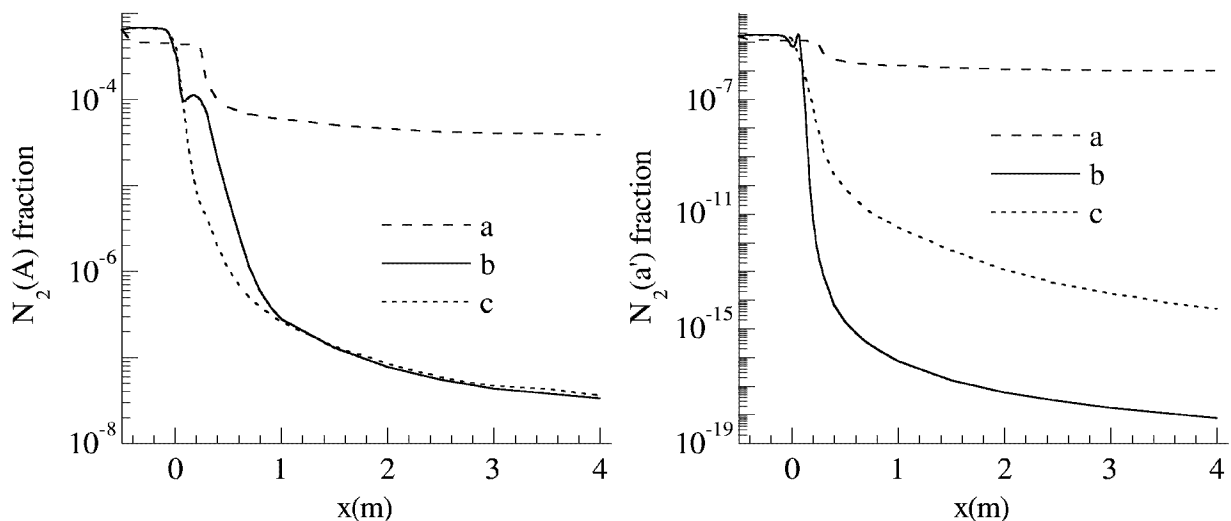
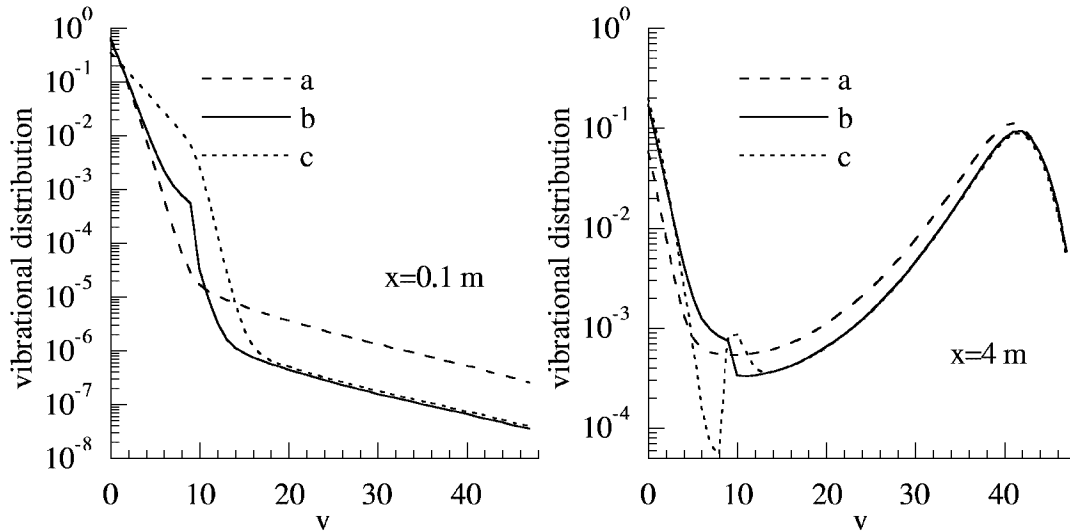


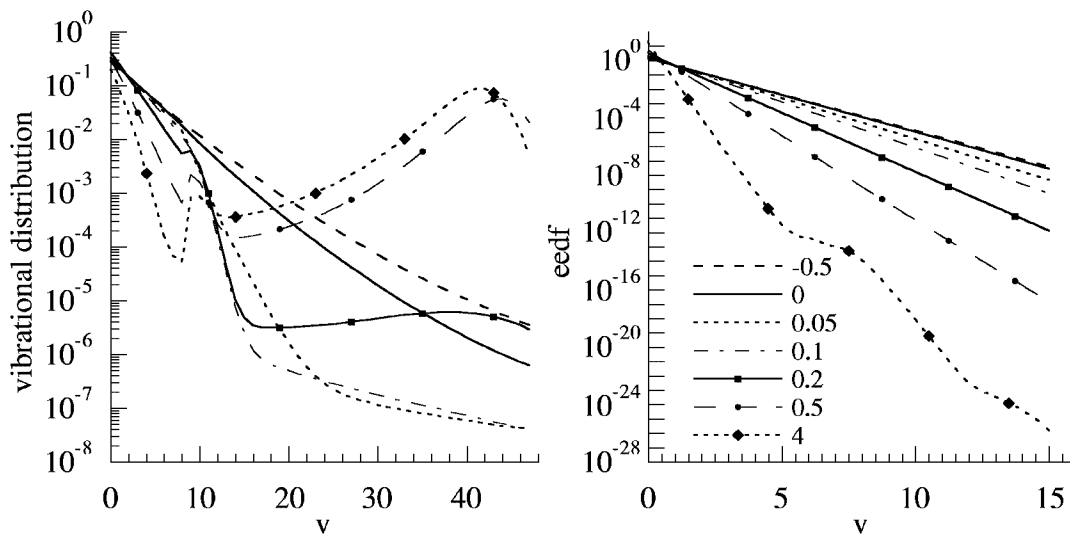
FIGURE 4.  $N_2(A)$  and  $N_2(a')$  molar fraction profiles calculated for different kinetic models; a proc 10-15, b proc 10-36, c proc 8-36.

Inclusion of processes 16-36 in the kinetics has dramatic effects not only on the electronically excited states (see fig 4), but also on the vibrational distributions (see fig. 5) mainly for vibrational quantum numbers  $v > 10$ . The molar fraction of  $N_2(A)$  is influenced by e-M collisions only in the region close to the throat ( $0 < x < 1$  m). When e-M collisions are neglected (fig 4, curve b), the fraction of  $N_2(A)$  is larger than in the case in which they are considered (fig 4, curve c). In the first case (b) the recombination of atoms in the state  $N_2(A)$  produces a peak around 0.2 m, that disappears when e-M collisions are considered (case c) because electronic superelastic collisions dominates over all the processes. For  $x > 1$  m the molar fraction is not affected by the presence of e-M collisions because the dominant processes are the quenching of  $N_2(A)$  by atoms and molecules and atom recombination. The state  $N_2(a')$  behaves differently; e-M collisions induce higher population than in case b, due to inelastic collisions in the region close to the throat and the differences remain constant for  $x > 1$  m.

These behaviours are reflected on the vibrational distributions (see fig 5). Close to the throat ( $x=0.1$  m), e-M collisions dominate (in particular inelastic e-v) for  $v < 10$  and therefore the vibrational distribution in this case is more populated than in the other cases, on the contrary the distribution tail is determined by the competition between the atom recombination and the vibrational-electronic coupling processes. At the nozzle exit ( $x=4$  m) the distribution tails are populated by the recombination, while for  $v < 10$  the superelastic vibrational collisions reduce the distribution energy.



**FIGURE 5.** Vibrational distributions in two different nozzle position calculated in different kinetic models; a proc 10-15, b proc 10-36, c proc 8-36.



**FIGURE 6.** Vibrational distributions along the nozzle calculated for model c (proc 8-36).

To complete the analysis of the system, in figure 6 vibrational and electron distributions are reported for different positions. The two distributions present different relaxations. Vibrational distribution cools down for  $x < 0.1$  m, and for  $x > 0.1$  m the recombination becomes very efficient and the tails are populated. Past the throat all the distribution are non Boltzmann. The eedf has an opposite trend. For  $x < 0.1$  m eedf relaxes very slowly, and only for  $x > 0.2$  m the relaxation speeds up. Moreover, the

distributions are almost maxwellian till  $x=0.5$  m, and only at long distance the eedf presents some plateaux, a characteristic sign of the presence of superelastic electronic collisions.

## CONCLUSIONS

In this work we have shown that the relaxation of the vibrational and electron distributions depends on the kinetic model considered; electronically excited states are strongly coupled to vibrational kinetics and electron kinetics. For this reason self-consistent models become the only tool to properly describe plasma kinetics. The model can be easily extended to investigate plasma jets, considering the effects the electric fields produces on the kinetics. The results reported in the present paper are qualitatively similar to those presented in other works [6,7], but present differences due to the nozzle geometry. The model should be extended to air mixtures for application to hypersonic wind tunnels and to collisional-radiative models of atomic species to investigate the expansion of a plasma produced by laser ablation [27].

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## REFERENCES

1. G.Colonna, M.Tuttafesta, M.Capitelli, D.Giordano, *Rarefied Gas Dynamics* (vol 2) Ed. R.Brun et al., 1999 281-288.
2. G.Colonna, M.Tuttafesta, M.Capitelli, D.Giordano, *JTHT* **13**, 372-375, (1999).
3. G.Colonna, M.Tuttafesta, M.Capitelli, D.Giordano, AIAA 99-3685, 1999 and *JTHT* **14**, 1-3 (2000).
4. G.Colonna, C.Gorse, M.Capitelli, R.Winkler, J.Wilhelm, *Chem. Phys. Lett.* **213**, 5-9, (1993) .
5. G.Colonna, M.Capitelli. *JTHT* **10**, 406-412, (1996).
6. G.Colonna, I.Armenise, M.Catella, M.Capitelli, *J. Tech. Phys.* **41** (special issue) 203-214 (2000).
7. G.Colonna, M.Capitelli, AIAA 2000-2415 (2000).
8. G.Colonna, M.Tuttafesta, M.Capitelli, D.Giordano, *JTHT*, **13**, 372-375.
9. S.D.Rockwood, *Phys. Rev. A* **8**, 2348 (1973)
10. G.Colonna, M.Capitelli, *JTHT* **10** No 3 (1996) 406-412.
11. G.Capriati, G.Colonna, C.Gorse, M.Capitelli, *Plasma Chem Plasma Proc.* **12** No 3, 237-260 (1992).
12. C.Gorse, M.Capitelli, *J. Appl. Phys.* **62** No 10, 4072-4076 (1987).
13. A.Garscadden, N.Rajesh, *Plasma Sources Sci. Technol.* **4**, 268-280 (1995).
14. B.Gordiets, C.M.Ferreira, M.J.Pinheiro, A.Ricard, *Plasma Sources Sci. Technol.* **7**, 207 (1992).
15. I.A.Kosy, Y.A.Kostinsky, A.A.Matveyev, V.P.Silakov, *Plasma Sources Sci. Technol.* **1**, 268-280 (1995).
16. F.Debal, J.Bretagne, M.Jumet, M.Wautelet, J.P.Dauchot, M.Hecq, *Plasma Sources Sci. Technol.* **7**, 219-229 (1998).
17. P.A.Sá, J.Loureiro, *J. Phys. D: Appl. Phys.* **30**, 2320-2330 (1997)
18. S.N.Nahar, A.K.Pradhan, *The Astrophys. J. Suppl Series* **111**, 339-355 (1997).
19. M.Cacciatore, M.Capitelli, C.Gorse, *Chem. Phys.* **66**, 141-151 (1982).
20. M.Capitelli and R.Celiberto, *Novel Aspects of Electron-Molecule Collisions*, Ed. K.H. Becker, World Scientific Publishing Co. Pte. Ltd. 1998, 283-323
21. W.M.Huo, T.L.Gibson, M.A.P.Lima, V.McCoy, *Phys. Rev. A* **36** No 4, 1632-1641 (1987).
22. A.V.Phelps, L.C.Pitchford, *JILA report No 23*, University of Colorado, Boulder Colorado (1985).
23. M.Allan, *J. Phys. B: At. Mol. Phys.* **18**, 4511-4517 (1985).
24. L.A.Morgan, *J. Phys. B: At. Mol. Phys.* **19**, L439-L445 1986).
25. D.Ton-That, M.R.Flannery, *Phys. Rev. A* **15**, 517-526 (1977).
26. L.Dubé, A.Herzenberg, *Phys. Rev. A* **20**, 194-213 (1979).
27. G.Colonna, D.Pietanza, M.Capitelli, RGD 2000, paper No 13015