An Investigation on the Role of Rotational Mechanisms in Electron Swarms at Low Reduced Electric Field in N_2, O_2 and H_2

M. A. Ridenti[1], L. L. Alves[2], V. Guerra[2], J. Amorim[1]

[1]*Departamento de Fìsica, Instituto Tecnológico de Aeronáutica, 12228-900, São José dos Campos, Brazil.*
[2]*Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*

The swarm of electrons in N_2, O_2 and H_2 was described in the low field regime (10^{-4} − 10 Td) by solving the homogeneous Boltzmann equation under the classical two-term approximation. Elastic, vibrational and rotational electron-neutral encounters were included in the collisional operator. Three different approaches were adopted to describe the rotational excitation / de-excitation: the discrete inelastic / superelastic collisional operator, written for a number of rotational levels that depends on the molecular gas and the specific rotational cross sections considered; the continuous approximation for rotations; and a modified version of the continuous approximation for rotations, including a Chapman-Cowling corrective term proportional to the gas temperature. The expression of the rotational collision operator for this latter approach is deduced here, and results show that it bridges the gap between the discrete and the continuous descriptions at low / intermediate reduced electric fields. Calculations are compared with measurements for the available swarm parameters, to assess the validity of the different approaches and cross sections adopted to describe rotational mechanisms.

1. Introduction

Plasmas produced in nitrogen, oxygen and hydrogen, in pure form or as mixture components often in combination with noble gases, are the focus of a wide-range of interests spanning from fundamental studies to applications in various fields, such as material processing and functionalization, biomedical purposes, and environmental / energy applications [1,2], among others. In molecular gas discharges running at very-low *E/N* (*E* is the electric field and *N* is the gas density) electron-neutral rotational and vibrational collisions are competitive enough to become important energy-transfer channels [3], influencing the electron energy distribution function (EEDF) and the corresponding swarm parameters. In the early studies of the electron kinetics in molecular gases [4,5], computational limitations hampered the accounting of electron-neutral rotational excitations / de-excitations for a large number of rotational levels at intermediate reduced electric fields. Some approximations were developed to treat these cases, such as the *continuous approximation for rotations* [4] (CAR) and the *single level approximation for rotations* [5] (SLAR).

In this work, the homogeneous electron Boltzmann equation (EBE), written under the classical two-term approximation [6,7], is solved in N_2, O_2 and H_2 for reduced electric fields in the interval 10^{-4} − 10 Td. A code based on previous works [8-10] was especially developed for this purpose, adopting three different approaches to describe electron-neutral rotational excitations / de-excitations: (i) using the discrete inelastic / superelastic collisional operator, written for a number of rotational levels that depends on the molecular gas and the specific rotational cross sections considered; (ii) replacing the discrete collisional operator for rotations by the CAR expression, deduced for the set of rotational cross sections proposed by Gerjuoy and Stein [3]; (iii) generalizing the CAR expression to include a "Chapman-Cowling term" proportional to the gas temperature T_g [11], similarly to what is usually adopted for the elastic collision operator [12], trying to bridge the gap between approaches (i) and (ii) for low / intermediate *E/N* values at various T_g. To assess the validity of these approaches and of the rotational cross sections adopted for the different gases, calculation results are compared with measurements for the available swarm parameters, namely the electron mobility and the electron characteristic energy.

2. Formulation

2.1. The homogeneous Boltzmann equation

The present study is based on the solution to the homogeneous EBE for a stationary case, written as a continuity equation for the total electron flux in energy space $G = G_E + G_c$ [6,7]

$$\frac{d(G_E+G_c)}{du} = \Im \,. \qquad (1)$$

Here, G_E and G_c are the electron fluxes in energy space driven by the electric field and caused by electron-neutral elastic collisions, and $\Im$ is the net electron creation rate, in energy interval *du* and per unit time, due to inelastic / superelastic collisions

$$\Im = \sqrt{\frac{2e}{m}} \sum_{s,j,j'} n_s \{ \delta_{s,j} [(u + u_{s,jj'}) \sigma_{s,jj'} (u + u_{s,jj'}) f(u+u_{s,jj'}) - u \sigma_{s,jj'}(u) f(u)] + \delta_{s,j'} [(u - u_{s,jj'}) \sigma_{s,j'j} (u - u_{s,jj'}) f(u - u_{s,jj'}) - u \sigma_{s,j'j}(u) f(u)] \} . \quad (2)$$

In (2), u is the kinetic energy in eV; e and m are the electron charge and mass, respectively; f is the EEDF satisfying $\int_0^\infty f\sqrt{u}\,du = 1$; $\delta_{s,j}$ is the relative density of sublevel j of species s; $\sigma_{s,jj'}$ and $\sigma_{s,j'j}$ are the electron-neutral scattering cross section for the excitation / de-excitation between sublevels j' and j of state s, with energy threshold $u_{s,jj'}$. For the low values of E/N under investigation, the collisional operator may be decomposed as

$$\Im = \Im_{vib} + \Im_{rot} , \quad (3)$$

and the part relative to rotations $\Im_{rot}$ can be written under continuous form, when the electron characteristic energy is much larger than the thermal energy, with electrons exchanging only little energy after each collision event. This is the framework of the CAR, whose expression is [3]

$$\Im_{rot} = -\frac{d}{du}\left(N\sqrt{\frac{2e}{m}} 4\sigma_0 B u f \right), \quad (4)$$

with B the rotational constant and $\sigma_0 \equiv 8\pi Q^2 a_0^2/15$ (Q is the quadupole moment constant and a_0 is the Bohr radius). The derivation of (4) is based on the first-order Taylor expansion of (2). A second-order expansion of the same equation, applicable at low/intermediate E/N values, gives *the Chapman-Cowling correction to the CAR* (CC-CAR)

$$\Im_{rot} = -\frac{d}{du}\left[N\sqrt{\frac{2e}{m}} 4\sigma_0 B u \left(f + \frac{k_B T_g}{e}\frac{df}{du} \right) \right]. \quad (5)$$

2.2. Collisional data

The rotational excitations are described here using either a discrete or a continuous approach. In general, the collisional data are taken from the IST-LISBON database with the website LXCat [13].

For nitrogen and oxygen, the discrete collisional operator is written adopting the rotational cross sections of either Gerjuoy and Stein [3] or of Oksyuk [14] for the $J \rightarrow J + 2$ transitions with J = 0,1,2,…,30 in N_2 and J = 1,3,5,…,30 in O_2. In hydrogen, polarization, exchange and short-range interaction mechanisms are expected to affect significantly the rotational cross sections. In this case, the discrete collisional operator is based on a different set of rotational cross sections [13], which was originally constructed following the recommendations of Tawara *et al.* [15].

3. Results and discussion

The calculations are performed adopting an energy-grid step smaller than the lowest rotational energy threshold. Typically, the solver uses energy grids with 6000-8000 points at maximum energies u_{max} = 1.2 – 10 eV, depending on the E/N values.

Figure 1(a)-(b) presents the electron reduced mobility μN and the characteristic energy u_k, respectively, as a function of the reduced electric field, calculated and measured in nitrogen at T_g = 300 K, 195 K and 77 K. Results show that using the analytical cross sections proposed either by Gerjuoy and Stein [3] or by Oksyuk [14], as rotational input data in a two-term Boltzmann solver, gives predictions of swarm parameters for N_2 that are consistent with measurements. For E/N > 0.5 Td, the swarm parameters calculated with the Oksyuk cross sections exhibit higher deviations with respect to measurements, reaching 12% for μN and 20% for u_k. The analysis of the electron power transfer reveals that using the Oksyuk cross sections leads to higher rotational energy losses above 0.1 Td. Overall, the simulations demonstrate that the CC-CAR is able to bridge the gap between a discrete and a continuous description of rotational collisions, for low / intermediate E/N values at various T_g, which is not possible when using the CAR.

Figure 2(a)-(b) shows the results in oxygen. Again, good agreement between measurements and calculations is found, using both the discrete collisional operator for rotations and the CC-CAR.

Figure 3(a)-(b) shows μN and u_k, respectively, as a function of E/N, calculated and measured in hydrogen at T_g = 300 K and 77 K. Results show that predictions, calculated using the discrete collisional operator for rotations with the IST-LISBON dataset, are in good agreement with swarm measurements available. Note that using exclusively the Gerjuoy and Stein cross sections, for all $J \rightarrow J + 2$ transitions (J = 0,1,2,...,20), yields results that deviate from the ones obtained with the IST-LISBON dataset, for $E/N > 10^{-2}$ Td. Contrary to what is observed in N_2 and in O_2, calculations using the CC-CAR in H_2 are not able to reproduce the predictions of the discrete formulation, for $E/N \cong 10^{-2} - 1$ Td and T_g = 300 K and 77 K. This is due to the large rotational characteristic temperature of H_2, $\Theta_{rot} \cong 84.6$ K, associated with rotational excitation energies higher than the thermal energy $k_B T_g/e$.

4. Final remarks

This work has analysed the role of rotational mechanisms in the electron kinetics of diatomic homonuclear gases, at low / intermediate reduced

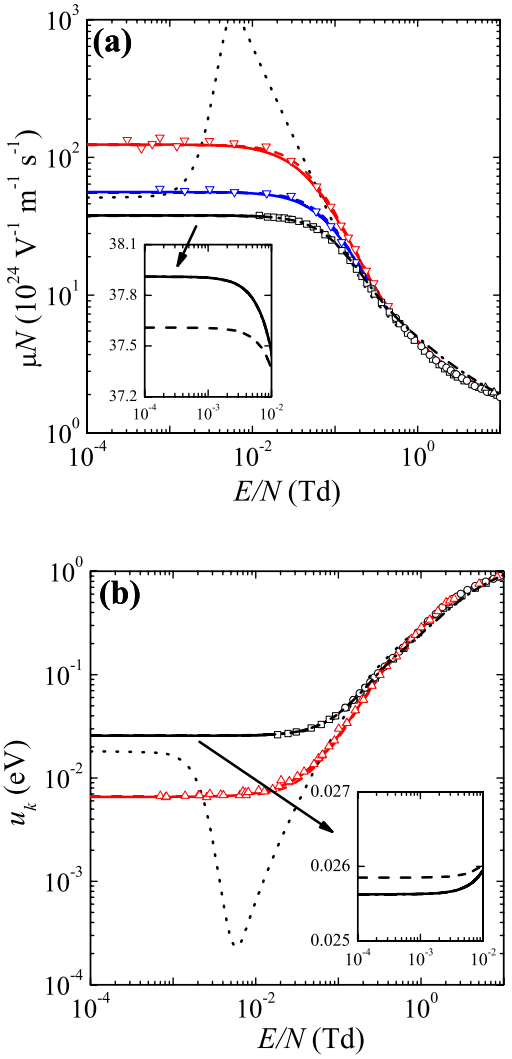

Figure 1: Electron swarm parameters in nitrogen, as a function of the reduced electric field, for T_g = 300 K (black), 195 K (blue) and 77 K (red). The lines are calculation results obtained using: Gerjuoy-Stein [3] (solid) or the Oksyuk [14] (dashed-dotted, 300 K only) cross sections; CC-CAR (dashed); CAR (dotted). (a) Reduced mobility. The points are measurements from: Lowke [16] (□); Nakamura [17] (○); Snelson and Lucas [18] (△); Pack and Phelps [19] (▽, 195 K and 77 K). (b) Characteristic energy. The points are measurements from: Crompton *et al.* [20] (□); Jory [21] (○), Warren and Parker [22] (△).

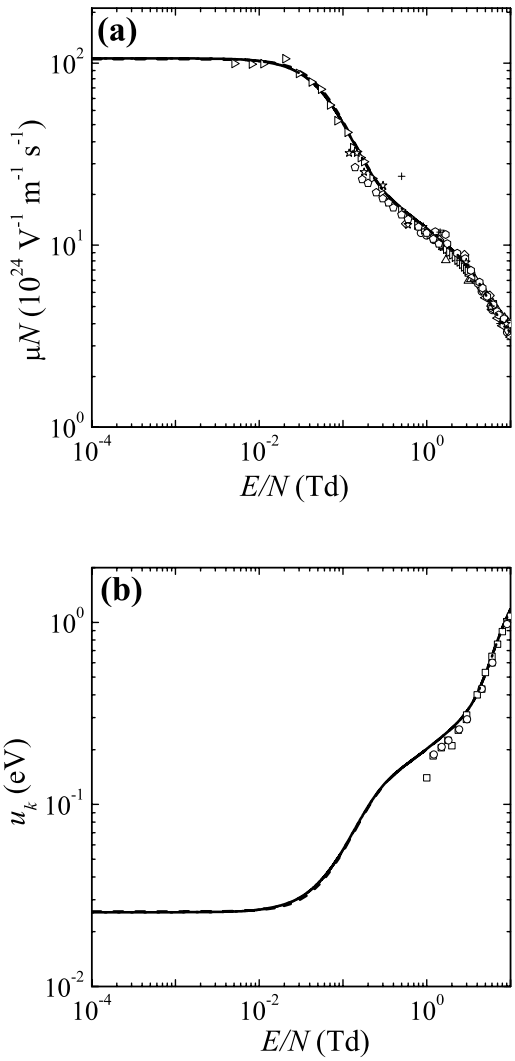

Figure 2: Electron swarm parameters in oxygen, as a function of the reduced electric field, for T_g = 300 K. The lines are calculation results obtained using: Gerjuoy-Stein [3] (solid) or the Oksyuk [14] (dotted) cross sections; CC-CAR (dashed). (a) Reduced mobility. The points are measurements from: Brose [23] (□); Crompton and Elford [24] (○); Doehring [25] (△); Fleming *et al.* [26] (▽); Herreng [27] (◇); Jeon and Nakamura [28] (◁); Nelson and Davis [29] (▷); Nielsen and Bradbury [30] (⬭); Pack as given in [5] (☆); Reid *et al.* [31] (⌂); Roznerski and Leja [32] (+). (b) Characteristic energy. The points are measurements from: Fleming *et al.* [26] (□); Rees [33] (○).

electric fields. Results showed very good agreement between calculations and measurements of the available swarm parameters, for N_2, O_2 and H_2 at the different gas temperatures considered, when adopting the discrete collisional operator for rotations. For N_2 and O_2, the CC-CAR can also give predictions of swarm parameters consistent with measurements. The CC-CAR expression bridges the gap between a discrete and a continuous description of rotational collisions, for low / intermediate *E/N* values at various T_g, thus corresponding to an alternative approach to describe electron-neutral rotational excitations / de-excitations with minimal numerical complications.

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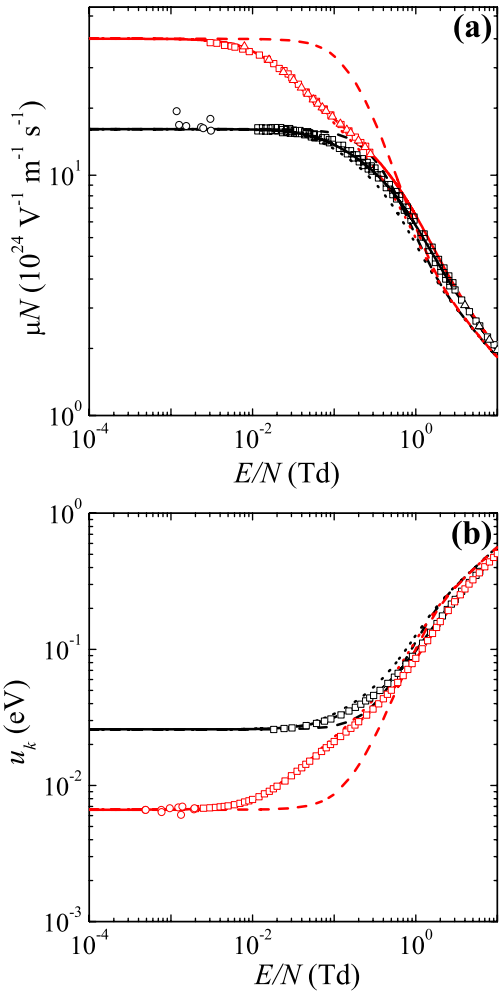

Figure 1: Electron swarm parameters in hydrogen, as a function of the reduced electric field, for T_g = 300 K (black) and 77 K (red). The lines are calculation results obtained using: IST-LISBON [13] (solid) or the Gerjuoy-Stein [3] (dotted) cross sections; CC-CAR (dashed). (a) Reduced mobility. The points are measurements from: Lowke [16] (□, 300 K and 77 K; ⊞, 293 K); Pack and Phelps [19] (○); Robertson [34] (△). (b) Characteristic energy. The points are measurements from: Crompton et al [35] (□); Warren and Parker [22] (○, 77 K).

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