Role of molecular ions in plasmas of atmospheric and energetic interest

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Abstract. Molecular ions often play a very important role in plasmas. The electron energy distribution function \( (eedf) \) and density \( (n_e) \) are influenced by the reactions of molecular ions with electrons. We bring these aspects into focus by studying successively the following situations: We show that the dissociative recombination of \( \text{Ar}^+_2 \) allows to understand the measured characteristics of an argon supersonic plasma flow where the electron density is low. Afterwards, we show the dominating role of \( \text{NO}^+ \) in the chemistry of a space vehicle atmospheric re-entry air plasma. Finally, by using the Boltzmann equation in order to show the influence of molecular ions such as \( \text{NO}^+ \) in air plasmas on the \( eedf \), we comment on the common assumption of Maxwell-Boltzmann equilibrium for this distribution.

1. Introduction

The interest in plasmas is greater than that illustrated by the vast number of fields and studies. Plasmas can be found at the intersection between fluid mechanics, thermodynamics, chemistry, radiative transfer and atomic and molecular physics. This peculiarity is mainly due to the presence of electrons, obtained by high temperature and/or electric fields, leading by inelastic collisions to the production of excited and ionized species. This is the reason why some of the key parameters for experimental or modelling studies in plasma physics are the electron characteristics such as the electron energy distribution function \( (eedf) \) and density \( (n_e) \). They are both greatly influenced by the ionic species (which are as numerous as electrons due to the electro-neutrality) since the cross sections of most of the possible processes are high due to the Coulombic aspect of the interaction.

We propose to bring these aspects to light in the case of molecular ions by studying the following situations. In order to explain the unexpectedly low \( n_e \) and the high population density of the highly excited levels measured in an argon plasma, we develop in a first part a collisional-radiative (CR) model devoted to the thorough study of its chemical behavior. In spite of the low pressure of the flow and although in atomic plasmas the molecular ions are not often formed in usual situations, we show that the presence and the chemistry of \( \text{Ar}_2^+ \) mainly driven by the dissociative recombination (DR) are enough to understand the measured characteristics.

In a second part, we develop another CR model devoted to the chemical study of the air plasma resulting from the atmospheric re-entry of a space vehicle. The plasma so produced being far from equilibrium and inducing high energy flux densities at the thermal shield, the kinetic scheme has to be particularly well complete. The CR model accounts for a great number of species and processes in order to work over a wide range of pressure and temperature conditions. The contribution of energy relaxation at the wall of the excited and dissociated species may be important and the electron processes
play an important role in their chemistry. We put forward, among the ionic species taken into account, the dominating role of NO\(^+\) by its DR with electrons.

In plasma modelling, the usual assumption of Maxwell-Boltzmann equilibrium leads to the concept of temperature for electrons as well as heavy species. In a last part, we discuss this hypothesis adopted in our CR model in air by solving the Boltzmann equation for electrons. Despite the possible high heavy particle temperature leading to a high rate coefficient for associative ionization, we show that the DR of NO\(^+\) may yield discrepancies for moderate electron energy preventing the distribution from being Maxwellian.

2. Balance equation

Except for the last part of this communication devoted to the Boltzmann equation, our main purpose is related to the plasma flows with the velocity \(\vec{v}\) and especially to the treatment of the balance equation for a given species \(X\) on the excited level \(i\) in Lagrangian description [1]:

\[
\frac{D[X_i]}{Dt} + [X_i] \vec{\nabla} \cdot \vec{v} = -\vec{\nabla} \cdot \vec{J}_{Xi} + \left[ \frac{\partial [X_i]}{\partial t} \right]_{CR}
\]

where \(D[X_i]/Dt\) is the hydrodynamic derivative characterized by the time scale \(\tau_{HD}\), the second term accounts for the influence of the fluid expansion or contraction (time scale \(\tau_{PEC}\)), \(-\vec{\nabla} \cdot \vec{J}_{Xi}\) results from the diffusion of the species (characteristic time \(\tau_i\)) of which the flux density is \(\vec{J}_{Xi}\) and the term with the index “CR” is the source term of the balance equation due to the collisional and radiative processes.

In reactive flows with high velocity, \(\tau_{HD}\) is usually less than \(\tau_{PEC}\) and \(\tau_i\) so that the relevant processes to be involved in the source term of (1) have to be characterized by a time scale less or equal \(\tau_{HD}\). The situation is then intermediate between a frozen flow where the collisional and radiative processes related to \(X_i\) are completely inoperative and the equilibrium situation where \(X_i\) depends on the local conditions (pressure and temperature) only: The flow is therefore in chemical disequilibrium.

The elaboration of a CR model consists in fact in the thorough calculation of the source term of the previous balance equation for each involved species. Among them, the molecular ions play an important role. The relevant processes to be considered in this term have to be associated with a sufficiently short time scale and we describe briefly the CR model for argon and air in the subsequent parts of this paper.

3. Argon supersonic plasma flow

In a inductively coupled plasma (ICP) torch, van Ootegem [2] has studied a highly expanded and weakly ionized plasma at relatively high pressure in order to investigate the electron density fluctuations in the

| Table 1. CR models considered for comparison with experimental results obtained by van Ootegem [2] in a supersonic argon plasma. |
|_CR model| Species| Processes |
|---|---|---|
| 1| \(\text{Ar}(3p^6)\)| \(\text{Ar}_i \leftrightarrow \text{Ar}_f + h\nu\) |
| | \(\text{Ar}(3p^6)\)| \(\text{Ar}^+ + e^- \leftrightarrow \text{Ar}_i + h\nu\) |
| | \(\text{Ar}^+ (64 \text{ levels})\)| \(\text{Ar}_i + e^- \leftrightarrow \text{Ar}_f + e^-\) |
| | \(\text{Ar}^+ (64 \text{ levels})\)| \(\text{Ar}^+_i + e^- \leftrightarrow \text{Ar}^+_f + 2e^-\) |
| | \(\text{Ar}^+ (64 \text{ levels})\)| \(\text{Ar}^+_i + \text{Ar}(3p^6) \leftrightarrow \text{Ar}^+_f + \text{Ar}(3p^6)\) |
| | \(\text{Ar}^+ (64 \text{ levels})\)| \(\text{Ar}^+_i + \text{Ar}(3p^6) \leftrightarrow \text{Ar}^+_f + e^- + \text{Ar}(3p^6)\) |
| 2| \(\text{Ar}(3p^6)\)| The same than for the CR model 1 and: |
| | \(\text{Ar}(3p^6)\)| \(\text{Ar}^+ + 2\text{Ar}(3p^6) \rightarrow \text{Ar}^+_2 + \text{Ar}(3p^6)\) |
| | \(\text{Ar}^+ (64 \text{ levels})\)| \(\text{Ar}(3p^4s) + \text{Ar}(3p^4s) \rightarrow \text{Ar}^+_2 + e^-\) |
| | \(\text{Ar}^+ (64 \text{ levels})\)| \(\text{Ar}^+_2 + e^- \rightarrow \text{Ar}(3p^6/3p^4s) + \text{Ar}(3p^6)\) |
| | \(\text{Ar}^+_2\)| \(\text{Ar}^+_2 + e^- \rightarrow \text{Ar}^+_2 + \text{Ar}(3p^6) + e^-\) |
turbulent trailing wake of ballistic missiles. For the maximum energy available by the power supply, the electron parameters are a temperature of $T_e = (6000 \pm 500)$ K and a density of $n_e = (1.0 \pm 0.5) \times 10^{18}$ m$^{-3}$ near the nozzle exit where the flow is still laminar. The Ar excited level population densities were also determined exhibiting a Boltzmann equilibrium distribution following $T_e$. Conversely, Saha equilibrium is not fulfilled: Due to the value of $n_e$, the excited levels population density should be lower by a factor $10^3$ than the one obtained experimentally.

The hydrodynamic time scale of the flow being such that $10^{-6} < \tau_{HD} < 10^{-5}$ s, we have treated (1) neglecting $\vec{V} \cdot \vec{v}$ and $\vec{V} \cdot \vec{J}_X$ and developing two similar CR models [3]: The main difference consists of taking into account Ar$^+_2$ molecular ions and their relevant processes involved as shown in table 1. Figure 1 shows the results obtained by solving the balance equation for each species considering the CR model numbered 1 when the hydrodynamic derivative time scale $\tau_{HD}$ is reached. We can observe that the population densities are far from the experimental ones: an electron density of $3 \times 10^{19}$ m$^{-3}$ is needed to obtain the better agreement. The CR model 2 is more efficient in reproducing the measurement as we can see in figure 2. The Ar$^+_2$ number density is sufficiently high in the creation area of the plasma torch close to equilibrium with $p \simeq 16$ kPa and $T \simeq 9000$ K. Its DR leads to the formation of atoms in the $3p^54s$ metastable state which are excited afterwards by electron induced processes. These excited states are then found overpopulated with respect to the case of CR model 1 and consequently closer to the experimental situation. Figure 2 illustrates also the high sensitivity of the results to $n_e$ so that it is quite possible to obtain a better agreement by changing slightly the crucial basic data: The rate coefficient for DR or the branching ratio between the formation of atoms in their ground state or metastable states.

These were determined experimentally in the past in plasma conditions relatively far from those of the plasma jet studied here [4, 5] and should be revised for updating.

4. Space vehicle atmospheric re-entry air plasma

During spacecraft re-entry into the upper layers of the atmosphere, the relative stream is hardly slowed down and leads to the transition of the medium from the gas state to the plasma state inside a shock layer where the temperature can reach 12000 K. In order to know the composition of the plasma interacting with the fuselage and its excitation degree, we have elaborated a CR model involving 13 species: N$^+_2$, O$^+_2$, NO, N, O, N$^+_2$, O$^+_2$, NO$^+$, N$^+$, O$^+$, O$^+$, O$^-$ and electrons [6] working over a wide range of temperature and pressure. Processes similar to those already listed for argon have been considered for the present species. We have paid particular attention to the DR of molecular ions especially that
of NO$^+$ for which extensive calculations of the cross section $\sigma_{\text{DR}}$ have been performed for vibrational excitation corresponding to $0 \leq v \leq 14$ using the Multichannel Quantum Defect Theory (MQDT) [7]. A thorough treatment of the results of Hellberg et al. [8] has allowed in addition a realistic estimation of the temperature dependent branching fractions.

For typical re-entry conditions ($p = 3 \text{kPa}$, $T = 6000 \text{K}$), figure 3 shows the time evolution of population density of the main species assuming negligible fluid expansion or contraction and diffusion in (1). The hydrodynamic derivative time scale being several $10^{-3} \text{s}$ for shock layer crossing, the relevant densities near the fuselage are those for $t \geq \tau_{\text{HD}}$: The plasma is clearly far from equilibrium and the dominant ion is NO$^+$ which recombines with electrons by DR. Adopting the particular re-entry conditions described by Park [9] for the stagnation zone in front of the spacecraft nose, we have calculated the spatial profiles of species without considering wall processes with the help of (1) where only the diffusion term is neglected (see figure 4). It is important to note that NO$^+$ is the dominating ion. It controls the electron density through electro-neutrality and accordingly the excited species density through inelastic collisions. A complete treatment of the balance equation has to be performed.

5. $e_{\text{edf}}$ in a re-entry air plasma

The CR model displayed in section 4 is based on the hypothesis of equilibrium of the kinetic energy of electrons and heavy species. In fact, many processes influence the final value of the $e_{\text{edf}}$, denoted $f$ [10]. They are taken into account in the terms $P$ and $N$ of the Boltzmann equation

$$\sqrt{\varepsilon} \frac{\partial f(\varepsilon)}{\partial t} = P - N,$$

where $P$ is the differential frequency corresponding to processes increasing the population of electrons with energy $\varepsilon$ and $N$ the analogue for a decrease of this population. For DR, $N$ is given by $n_e \sqrt{2/m_e} \sigma_{\text{DR}}(\varepsilon) f(\varepsilon)$ with $m_e$ the electron mass. In the typical recombining conditions of figure 4, the time scale for reaching the steady state $e_{\text{edf}}$ is $10^{-8} \text{s}$ so that the $e_{\text{edf}}$ is in steady state at each location. NO$^+$ is the predominant ion. The effect of its DR is to lead to depletion of the distribution for $\varepsilon$ lower than 4 eV (the DR cross section being higher than $10^{-20} \text{m}^2$ in this case [11]). Although the energy range is rather small, this depletion may cause a disequilibrium in the vibrational distribution since the energy range is the same. In addition, the electron-electron collision frequency may decrease: Elastic collisions between electrons and heavy particles may become predominant preventing a Maxwellian $e_{\text{edf}}$ [12].
6. Conclusion

Three aspects of the influence of molecular ions were studied in this communication for the case of atomic and molecular plasmas. They show the difficulty of performing realistic modelling of this kind of media and the necessity to have reliable and accurate cross sections and branching fractions. Conversely, they illustrate the possibility to verify indirectly these data by their effect on electron and heavy particle distributions.

Acknowledgments

The authors wish to thank Dr Anne Bourdon for the collaboration between institutions (CORIA and EM2C, Ecole Centrale Paris, France) having made the elaboration of the CR model for argon and air. The authors wish to thank also Prof Ioan F Schneider from LMPG, University of Le Havre, France, for the ever interesting and fruitful partnership in many fields of plasma physics.
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