Electron-molecule collision processes in non-equilibrium molecular plasmas

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The role of internal degrees of freedom of molecular species in non-equilibrium plasmas is briefly outlined. Importance of collision cross sections for electron-impact with excited molecules in kinetic models is discussed, and few examples of some particular process in real plasma systems is illustrated. Some preliminary results of vibrational excitations by electron impact are shown.

The presence of molecular species in a plasma system, give rise to an enormous number of collisional processes which make the description of the microscopic physics and the formulation of theoretical models a quite complex task. This comes from the fact that the molecules are distributed among their electronic states, each supporting, when of bound nature, a number of vibrational and rotational levels. Each molecule in a given quantum states, acts in the plasma independently of the other molecular states, yielding to its own collision processes and interactions, so that the number of *chemical species* explodes, becoming equivalent to the that of the molecular quantum states.

Electron-impact involving molecular species play a role of paramount importance in affecting the quantum state population. This is particularly true in those systems in non-equilibrium conditions, where Maxwell and Boltzmann distributions can result violated, and where inelastic and super-elastic electron-molecule collisions, besides the reactive channels leading to dissociation, ionization and recombination processes, can strongly contribute to the redistribution of the energy and, ultimately, to the macroscopic kinetic evolution of the system towards the stationary state.

A kinetic *ab initio* theoretical model of a non-equilibrium plasma, starts from the calculation of the collision cross sections for the processes occurring in the system. In particular, for electron-molecule collisions, these quantities will be calculated for a suitable range of incident electron energies, and for the relevant transitions linking, in principle, all the accessible quantum states of the molecules. This results in the need of huge sets of cross section data which require dedicated efforts for their production. Some simplification in general may occur in dependence on the plasma conditions. Few molecular electronic states can be involved in the processes and rotational transitions, in many situations, play a secondary role. On the other hand, vibrational excitations among the levels of the ground and excited electronic states, as a rule, cannot be neglected in a realistic and predictive description of a molecular plasma [1].

Several theoretical techniques have been formulated over the years for the calculation of the electron-molecule cross sections. Semiclassical and approximate quantum approaches are usually employed in dependence on the required accuracy and range of incident energies. Accurate quantum mechanical methods, however, become essential in the description of the low incident energy encounters, when the projectile-target interference effects become important.

Typical example of a molecular plasma, in non-equilibrium conditions, is provided by the hydrogen plasmas employed in thermonuclear fusion researches. In the divertor region of the tokamak reactor, in fact, where the plasma temperature is relatively low, H_2 molecule can condensate, giving rise to a large variety of collisional and radiative processes which strongly influence the system evolution. A second example of hydrogen fusion plasmas is given by the negative ion sources, designed for production and acceleration at high energies of negative H^- ions, aimed to the ignition of the fusion nuclear reactions. These sources are presently developed in view of the applications, as plasma heating devices, in the next generation fusion reactors of the ITER international project.

In both the above systems, the role of the vibrational levels can hardly be overestimated. In negative ion sources, for example, it is well known that the dissociative attachment, i.e. the main process leading to the production of gas-phase negative ions, occurs with a great efficacy from highly excited H_2 molecules. The aim of a kinetic model, becomes thus the identification of the best plasma conditions which may promote those processes leading to population increasing of the high vibrational levels.

As an example of two of the main e-H_2 processes, taking place in gas-phase, that can enhance the vibrational level concentration, beyond the Boltzmann distribution, we may mention the vibrational excitations occurring through the high-energy electron-impact, followed by radiative decay, and through the low-energy resonant scattering, namely:

$$e + \mathrm{H}_2(X^1\Sigma_g^+, v_i) \rightarrow \mathrm{H}_2(\text{excited singlet electronic states}) + e \rightarrow e + \mathrm{H}_2(X^1\Sigma_g^+, v_f) + \hbar\omega \quad (1)$$

$$e + \mathrm{H}_2(X^1\Sigma_g^+, v_i) \rightarrow \mathrm{H}_2^- \rightarrow e + \mathrm{H}_2(X^1\Sigma_g^+, v_f) \quad (2)$$

The first process, starting from the vibrational level v_i, involves intermediate electronic states, and so a relatively high electron energy is required to activate the transition. The excitation energy is then radiatively released and the molecule is left in an excited vibrational state v_f. The second process occurs through the formation of a resonant H_2^- molecular ion, by capture of the incident electron at low energies, whose re-emission leaves, again, the molecule in an excited vibrational level. The molecular ion can be in its ground or in one of its Rydberg excited electronic states.

These last resonant vibrational excitations, play a basic role also in the physics and chemistry of the planet's atmosphere in (re)entry conditions [2]. When a space vehicle impacts with the earth's atmosphere in the reentry stage at the supersonic speed, or enters that of an other planet, a shock wave is generate that heats by friction the surrounding gas. During the gas-vehicle interaction, the kinetic energy is transfered to the atmospheric components and complex physical and chemical processes may occur. In particular, the internal degrees of freedom of the molecular species can be activated so that their densities can thus strongly deviate from the Boltzmann distribution. A modeling of such systems, again requires a complete sets of state-to-state cross sections for all the chemical components of the atmospheric gas. A sample of resonant vibrational excitation cross sections, involving N_2 and NO molecules, occurring through the processes

$$\mathrm{N}_2(X^1\Sigma_g^+, v_i) + e \rightarrow \mathrm{N}_2^-(X^2\Pi_g) \rightarrow \mathrm{N}_2(X^1\Sigma_g^+, v_f) + e \quad (3)$$

$$\mathrm{NO}(X^2\Pi, v_i) + e \rightarrow \mathrm{NO}^-(^3\Sigma^-, ^1\Delta, ^1\Sigma^+) \rightarrow \mathrm{NO}(X^2\Pi, v_f) + e \quad (4)$$

is shown in the figure below for the vibrational transition $v_i = 10 \rightarrow v_f = 20$.

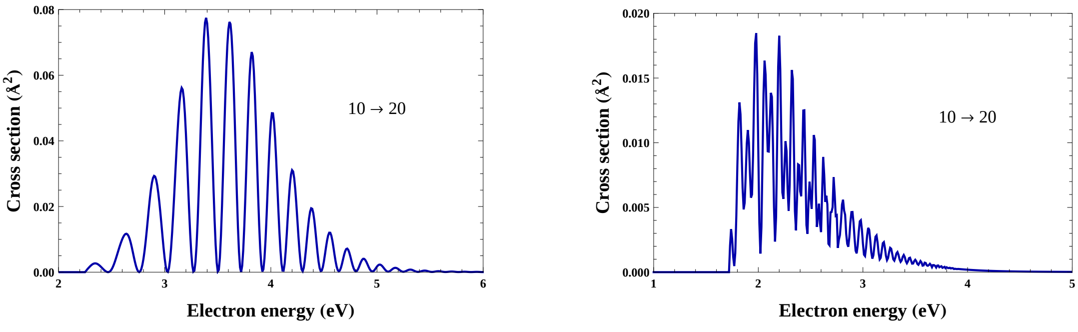

Fig. 1: Resonant vibrational excitation cross sections as a function of the electron energy for the processes (3) (left) and (4) (right).

Process (3) occurs through the shape resonance $X^2\Pi_g$, while three resonant states $^3\Sigma^-$, $^1\Delta$ and $^1\Sigma^+$ contribute to process (4).

The presentation will focus on electron-diatomic molecule collision cross sections, on their production, their physical aspects and their importance in relevant plasma systems of technological and scientific interest.

References

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[2] A. Bultel, B. G. Chéron, A. Bourdon, O. Metapon, I. F. Schneider, *Physics of Plasmas* **13**, (2006) 043502-(1-11).