

# Twenty Five Years of Vibrational Kinetics and Negative Ion Production in H<sub>2</sub> Plasmas: Modelling Aspects

M.Capitelli<sup>1,2</sup>, O.De Pascale<sup>2</sup>, P.Diomede<sup>1</sup>, A.Gicquel<sup>3</sup>,  
C.Gorse<sup>1</sup>, K.Hassouni<sup>3</sup>, S.Longo<sup>1</sup>, D.Pagano<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Bari, Bari, Italy*  
<sup>2</sup>*CSCP-IMIP(CNR), Sezione Territoriale di Bari, Bari, Italy*  
<sup>3</sup>*LIMHP-CNRS, Univerité Paris Nord, Villetaneuse, France*

## Abstract

Different approaches to study vibrational kinetics coupled to electron one for modeling different kinds of negative ion sources are presented. In particular two types of sources are investigated. The first one is a classical negative ion source in which the plasma is generated by thermoemitted electrons; in the second one, electrons already present in the mixture are accelerated by an RF field to sufficiently high energy to ionize the gas molecules. For the first kind of ion source a new computational scheme is presented to couple heavy particle and electron kinetics. Moreover models developed for an RF inductive discharge and for a parallel plate discharge are described.

## Introduction

The development of high current negative ion sources for generating intense neutral beams represents an important topic in the thermonuclear research field. Negative hydrogen ions are very important for the generation of neutral beams for heating magnetically confined fusion plasmas. Negative ion based neutral beam injector (N-NBI) is required because negative ion beams present a higher neutralization efficiency respect to positive ion ones at high energies<sup>1</sup>. Different kinds of negative ion sources are studied both from theoretical and experimental point of view, in order to optimize negative ion production. At present the volume plasma sources are widely used for H<sup>-</sup> generation, even though the addition of alkaline metals increases the concentration of negative ions.

## Vibrational Kinetics in H<sub>2</sub> Plasmas

Vibrational kinetics of molecular hydrogen under plasma conditions started his long way many years ago in an attempt to understand alternative mechanisms in the dissociation of H<sub>2</sub> under electrical discharges. Molinari and coworkers in an attempt to rationalize their experimental dissociation rates introduced the concept of a vibrational temperature higher than the translational one able to increase the dissociation of H<sub>2</sub> by heavy particle collisions<sup>2</sup>. This mechanism could prevail over the dissociation mechanism by electron impact in the cases in which this well known mechanism failed to describe the dissociation process. Capitelli *et al.*<sup>3</sup> building up a vibrational kinetic model mutated by the laser community first tried to implement the Molinari's ideas. The first model was very simple including the pumping of vibrational quanta through the e-V (electron-vibration energy exchange) processes and the redistribution of vibrational quanta on the vibrational ladder by V-V (vibration-vibration) and V-T (vibration-translation) energy transfer processes. V-V up pumping mechanism or Treanor's mechanism was able to bring the vibrational quanta up to the dissociation limit leading to dissociation rates higher than the dissociation rate induced by electron impact. This mechanism was called<sup>3</sup> a laser type mechanism or pure vibrational mechanism (PVM). This kind of name was given because the vibrational distribution of molecular hydrogen presented a long plateau typically met in CO lasers. The enthusiasm in the new mechanism was strongly damped when becomes clear that atomic hydrogen should be considered a killer of vibrational level populations. V-T deactivation of vibrationally excited hydrogen molecules, not considered in Ref.3, presented indeed large rates which strongly destroy the vibrational quanta

introduced by e-V processes. In a subsequent work the V-T term due to atomic hydrogen was inserted in the vibrational master equation having as result a strong decrease of the vibrational plateau and a consequent loss of importance of the pure vibrational mechanism in the dissociation process<sup>4</sup>. Only at very high electron density i.e. at high vibrational quanta pumping rates the pure vibrational mechanism could be effective in dissociating H<sub>2</sub> molecules. On the other hand large plateaux again arose as result of the recombination process which selectively pump vibrational quanta on the top of vibrational ladder.

Despite the strong deactivating effect of atomic hydrogen on the vibrational distributions of H<sub>2</sub> the research continued. In particular the authors of Ref.5 developed a joint vibrational dissociation mechanism (JVD) which included both the pure vibrational mechanism (PVM) and the electron impact dissociation (DEM) mechanism in the same model. Moreover the DEM model considered the dissociation transitions by electron impact from each vibrational level of vibrational ladder. The same authors realized the possibility of non-Maxwellian distribution functions for the electrons so that a Boltzmann equation for the electron energy distribution function (eedf) was solved to get the actual eedf. Soon after the importance of second kind collisions involving vibrationally excited H<sub>2</sub> molecules and electrons in affecting eedf was realized as well as the dependence of eedf on the presence of atomic hydrogen. For long time only superelastic vibrational collisions were considered in the kinetics; recently however two groups of research emphasized the role of metastable electronic states in forming structures in the eedf of H<sub>2</sub> plasmas.

At the same time a large effort was done to calculate electron impact dissociation and ionization cross sections involving each vibrational level of the H<sub>2</sub> vibrational manifold<sup>6</sup>, a problematic which is still under study nowadays<sup>7</sup>.

Three independent codes were built up in Europe mainly in Bari (Gorse<sup>8</sup>), Lisboa (Loureiro and Ferreira<sup>9</sup>) and Saint Petersburg (Baksht<sup>10</sup>). The research in the field shows a sharp increase when Bacal and Hamilton<sup>11</sup> discovered the presence of large concentrations of negative ions (H<sup>-</sup>) in multicusp magnetic plasmas. It was soon realized that the mechanism at the basis of the creation of negative ions in this kind of research was dissociative attachment from vibrationally excited molecules<sup>12</sup>. The relevant cross sections infact were shown to dramatically depend on the vibrational quantum number. The development of negative ion sources for fusion applications gives new impetus to the research in the field of vibrational kinetics in H<sub>2</sub> plasmas from both experimental and theoretical points of view. Different codes (Bari-Gorse<sup>13</sup>, Palaiseau-Bacal<sup>14</sup>, Livermore-Hiskes<sup>15</sup>, Japan-Fukumasa<sup>16</sup>) were built up to describe the complex phenomenology occurring in the plasma. In particular Hiskes<sup>17</sup> discovered a new elementary process for exciting the whole vibrational manifold of H<sub>2</sub> the so called E-V process which consists in the excitation of singlet electronically excited states of H<sub>2</sub> followed by radiative decay on the ground state. Corresponding cross sections first calculated by Hiskes have been then refined by Celiberto *et al.*<sup>18</sup>.

Different diagnostics were used to monitor the quantities entering in the model i.e. concentration of H, H<sup>-</sup>, H<sub>n</sub><sup>+</sup> species as well as electron number density and electron temperatures. At the same time sophisticated experiments were dedicated to measure the vibrational distribution (Essen-Dobele<sup>19</sup>), the eedf (Hopkins-Graham-Dublin<sup>20</sup>) and the ratio between cold and hot atomic hydrogen (Sultan-Orsay<sup>21</sup>). Atomic and molecular physics methods were also implemented to shed light on different elementary processes important to understand the physics of these discharges. In particular Laganà *et al.*<sup>22</sup> and Esposito *et al.*<sup>22</sup> presented complete sets of H-H<sub>2</sub>(v) rate coefficients, while Billing and Cacciatore<sup>23</sup> start their pionieristic work on the interaction of vibrationally excited states with copper surfaces and on the recombination of atomic hydrogen on the same surface. The last process indeed is important also for pumping vibrational energy in the molecules formed during heterogeneous recombination and finally desorbed by the surface. Atomic hydrogen changes his role from

being the killer of vibrationally excited molecules to being a source of them. On the other hand the experimental works of Hall *et al.*<sup>24</sup> and of Eenshuistra *et al.*<sup>25</sup> at the end of 1980s confirmed the production of vibrationally excited H<sub>2</sub> molecules during atom recombination thus starting a topics of large actuality at the present<sup>23</sup>.

It should be noted that the synergy between atomic/molecular physics and vibrational plasma kinetics has contributed to the advancement of negative ion production reactors. We believe indeed, that without the work of Wadehra and Bardsley<sup>12</sup> on the dependence of dissociative attachment cross sections on the vibrational quantum number and the work of Hiskes on the pumping of vibrational states by high energy electrons through the E-V process the concept of hybrid reactor for the formation of negative ions could not be probably developed. Nowadays another elementary process that one involving dissociative attachment on Rydberg states could push the negative ion community towards the development of other kind of reactors<sup>26-29</sup>.

Negative ion sources are still a fascinating topic in which vibrational kinetics constitutes one of the most important aspects.

At the beginning of 90s the H<sub>2</sub> plasma community was attracted to other kind of reactors those used in material science. In particular the microwave discharges used for the production of diamond films and parallel plate RF discharges for microelectronics acquired a noticeable technological importance. Also in this case two sophisticated codes were developed in Villateneuse<sup>30</sup> and Bari<sup>31</sup> for finding the optimum conditions in these reactors. At the same time a complete kinetic model was developed by Matveyev *et al.*<sup>32</sup> for describing high energy H<sub>2</sub> plasma expansion.

In the last 5 years a new impetus on vibrational kinetics arose for handling problems met by fusion people in the divertor plasma<sup>33</sup>. In particular the increase of ionic recombination assisted by vibrational kinetics at the edge of the divertor as well as the use of Monte Carlo simulation for H<sup>-</sup> ion and neutral transport are topics of current interest<sup>34,35</sup>.

In particular our team<sup>36-40</sup> is trying to improve the numerous input data entering in the kinetics describing the negative ion production in multipole, microwave and parallel plate reactors. Details of this modeling will be reported in the present lecture.

## Negative Ion Sources

Different methods can be used to generate plasmas. In this section we consider two different kinds of plasma sources that can be used to generate negative hydrogen ions.

In multicusp ion sources the plasma is produced by high energy electrons, emitted by hot filaments and accelerated by the negative voltage between the filaments and the source wall. The flux of accelerated electrons impinges on the H<sub>2</sub> target and gives rise to molecular and atomic reactions such as ionization, excitation and dissociation. In particular, negative ion production in the plasma volume is driven by the dissociative attachment of low energy electrons to highly vibrationally excited molecules. On the other hand high energy electrons cause H<sup>-</sup> destruction through electron detachment. This production mechanism evidences the necessity of dividing the source into two regions where electron energy distributions are optimized respectively for the plasma excitation and the dissociative attachment process. This separation is reached in multicusp ion sources by two kind of “filters”: the first one acts separating spatially electrons with different energies by means of a magnetic filter; the second one, realized pulsing the discharge (temporal filter), creates different electron energy distributions at different times.

Multicusp ion sources present some technical limitations due to the damage of the emitting filaments and their evaporation that causes also a contamination and then a variation in the operating conditions. These problems are absent in a RF discharge: because of their low mass,

electrons already present in the gas can be easily accelerated by the electric field to energies which are sufficient to ionize a gas molecule, then generating the plasma.

### Plasma Kinetic Modeling

In order to model kinetically a plasma and in particular a negative ion source we need to solve the vibrational kinetics of  $H_2(v)$ , the dissociation kinetics of  $H_2(v)$ , the kinetics of electronically excited states of  $H_2$  and  $H$ , the ion kinetics.

The time evolution of the heavy particle densities can be described by a set of nonlinear differential equations that reads as:

$$\begin{aligned} \left(\frac{dN_v}{dt}\right) = & \left(\frac{dN_v}{dt}\right)_{e-v} + \left(\frac{dN_v}{dt}\right)_{E-v} + \left(\frac{dN_v}{dt}\right)_{v-v} + \left(\frac{dN_v}{dt}\right)_{v-T} + \\ & \left(\frac{dN_v}{dt}\right)_{e-D} + \left(\frac{dN_v}{dt}\right)_{e-I} + \left(\frac{dN_v}{dt}\right)_{e-da} + \left(\frac{dN_v}{dt}\right)_{e-E} + \left(\frac{dN_v}{dt}\right)_{wall} \end{aligned} \quad (1)$$

where each term on the right hand side represents the gain or the loss for the  $v$ -th species due to a specific reaction and is given by:

$$\pm \left(\frac{dN_v}{dt}\right)_{TOT} = \sum_{i=1}^{react} \left( k_i \cdot \prod_{j=1}^{react} N_j \right) \quad (2)$$

where  $k_i$  is the rate coefficient for the  $i$ -th reaction and the product runs over the reactants for each reaction.

A complete description of the plasma kinetics of negative ion sources requires a self-consistent coupling between the heavy particle kinetics and the electron one. This coupling occurs as heavy particle density evolution depends on the rate coefficients of electron processes,

$$k_i^e = \int_{\varepsilon_{th}}^{\infty} \sigma_i(\varepsilon) v(\varepsilon) n(\varepsilon) d\varepsilon \quad (3)$$

which are themselves linked to the EEDF variations, however EEDF behaviour is strongly connected to the heavy particle distribution.

The EEDF is governed by the electron Boltzmann equation, which describes the time evolution of the electrons with energy between  $\varepsilon$  and  $\varepsilon + d\varepsilon$ . It takes into account of different terms involving the flux of electrons in the energy space due to various contributions. Some of the terms appearing in the Boltzmann equation are characteristic of the system we are investigating.

In the following paragraphs we describe three different models developed independently, but which apply the same state-to-state philosophy to describe the heavy particle kinetics.

#### Zero-dimensional Model of Multicusp Ion Sources

In multicusp ion sources the Boltzmann equation can be written as<sup>13</sup>:

$$\frac{\partial n(\varepsilon, t)}{\partial t} = - \left(\frac{\partial J_{el}}{\partial \varepsilon}\right)_{e-M} - \left(\frac{\partial J_{el}}{\partial \varepsilon}\right)_{e-e} + In + Ion + Sup + S - L \quad (4)$$

where  $-(\partial J_{el}/\partial \varepsilon)_{e-M}$  accounts for the flux of electrons along the energy axis due to elastic collisions,  $-(\partial J_{el}/\partial \varepsilon)_{e-e}$  for that due to electron-electron Coulomb collisions, and the other terms corresponds to inelastic ( $In$ ), ionizing ( $Ion$ ) and superelastic ( $Sup$ ) collisions and electron losses due to recombination. The term  $S$  characterizes the system under consideration and corresponds to the injection of electron through the hot filaments and reads as:

$$S = \frac{I}{Ve\Delta\varepsilon} \quad (5)$$

where  $I$  is the current of the injected electrons,  $V$  is the plasma volume and  $\Delta\varepsilon$  is the energy spreading of the injected electrons.

In previous works the coupling between heavy particle kinetics and electron kinetics was realized by solving at the same time step on the one hand the master equations describing the temporal evolution of the heavy particle density and on the other one the Boltzmann equation for the electron energy distribution function.

In this work we introduce a new approach<sup>40</sup> to couple heavy particle and electron kinetics, which shows a higher self-consistent character. In our scheme the electron energy range is discretized and represented by a set of intervals. At each interval, characterized by its mean energy, a different “kind” of electron is associated, then these “representative electrons” behave as the vibrationally or electronically excited levels of the hydrogen molecule or atom.

$$n(\varepsilon, t) \approx n(\varepsilon_i, t) \quad \text{for} \quad \varepsilon_i - \frac{1}{2}\Delta\varepsilon_i \leq \varepsilon \leq \varepsilon_i + \frac{1}{2}\Delta\varepsilon_i \quad (6)$$

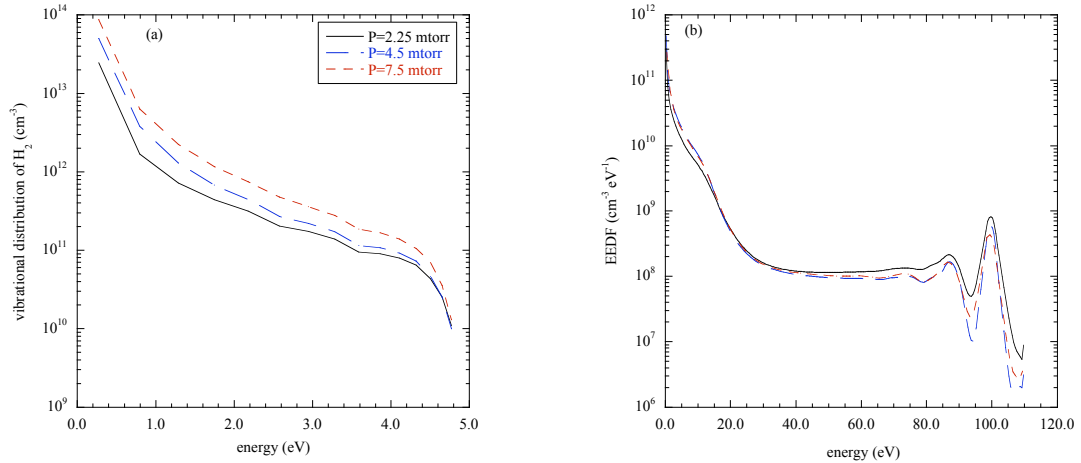
It means that also for electrons we can write a state-to-state set of kinetic equations whose rate coefficients can be written in the following way:

$$k_i^e = \sigma_i(\varepsilon)v(\varepsilon) \quad (7)$$

which represents the rate coefficient for the excitation of such a species promoted by an electron with velocity:

$$v(\varepsilon) = \sqrt{\frac{2\varepsilon}{m_e}} \quad (8)$$

These rate coefficients are no more global and referred to the overall electron energy distribution function but to an electron with a specific energy.



**Fig. 1. VDF (a) and EEDF (b) for different pressures ( $T_g=500$  K; discharge current=10 A; discharge voltage=100 V).**

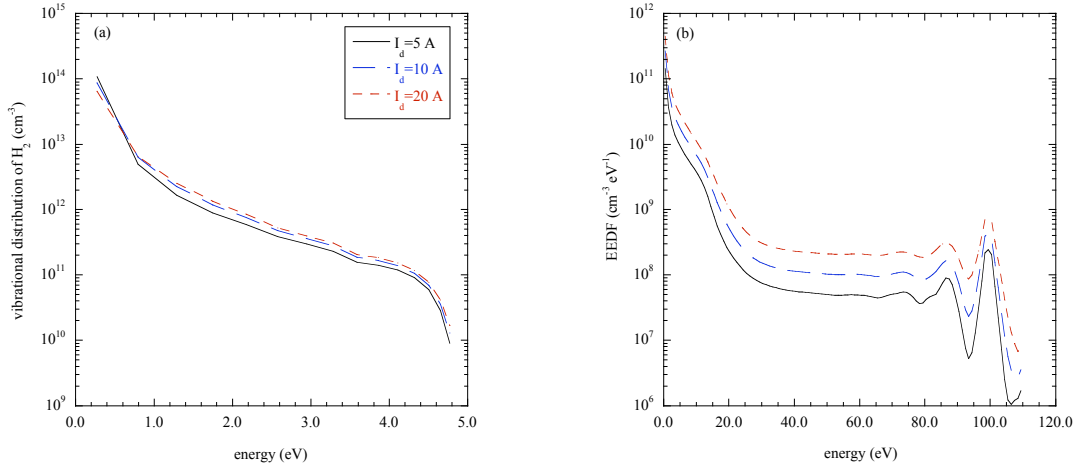
The described approach is easily applicable to all electronic processes, but it can be applied also to describe the flux of electrons along the energy axis due to elastic and electron-electron Coulomb collisions. Indeed, according to Rockwood<sup>41</sup> and Elliot *et al.*<sup>42</sup>, Boltzmann equation can be reformulated and terms due to these collisions can be rewritten and interpreted as the rate at which electrons are promoted or demoted between adjacent energy intervals.

The numerical scheme resulting from this approach has been used to build a zero-dimensional model of multicusp ion sources in the driver region. The negative ion

concentration is described as a function of some discharge parameters (pressure, discharge current) together with electron and heavy particle distributions.

Fig. 1a shows the vibrational distribution of H<sub>2</sub> as a function of the vibrational energy for different pressures: increasing the filling pressure, the number density of the vibrational levels increases; low vibrational levels are stronger affected by the increasing pressure. A pressure variation reflects on the plasma potential that governs the electron wall loss: the plasma potential decreases if the discharge current and the voltage current are kept constant. As a consequence the number of low energy electrons increases because they are not lost on the walls (Fig. 1b).

A variation of the discharge current does not cause a significant variation of the vibrational distribution of molecular hydrogen (Fig. 2a). On the other hand the electron energy distribution function is shifted at higher number density, reflecting the greater number of electrons injected from the filaments (Fig. 2b).



**Fig. 2. VDF (a) and EEDF (b) for different discharge current ( $T_g=500$  K; pressure=7.5 mtorr; discharge voltage=100 V).**

### ***RF Ion Sources: Microwave discharge***

Boltzmann equation assumes a slightly different form when we consider an RF discharge. In this case the source term  $S$  is lost, while another one appears, which describes the flux of electrons in the energy space due to the electric field (see Ref.41). Then Boltzmann equation reads as<sup>38,39</sup>:

$$\frac{\partial n(\varepsilon, t)}{\partial t} = - \left( \frac{\partial J_{el}}{\partial \varepsilon} \right)_{field} - \left( \frac{\partial J_{el}}{\partial \varepsilon} \right)_{e-M} - \left( \frac{\partial J_{el}}{\partial \varepsilon} \right)_{e-e} + In + Ion + Sup - L \quad (9)$$

The integration of the Boltzmann equation requires the determination of the RF electric field amplitude. This amplitude, or the corresponding root mean square (rms) value, can be determined from the absorbed RF power density that is a model input parameter known from the experiment. For this purpose, the following additional algebraic equation that expresses the dependence between the electric field and the absorbed RF power density (MWPD) was coupled to the electron Boltzmann and species balance equations:

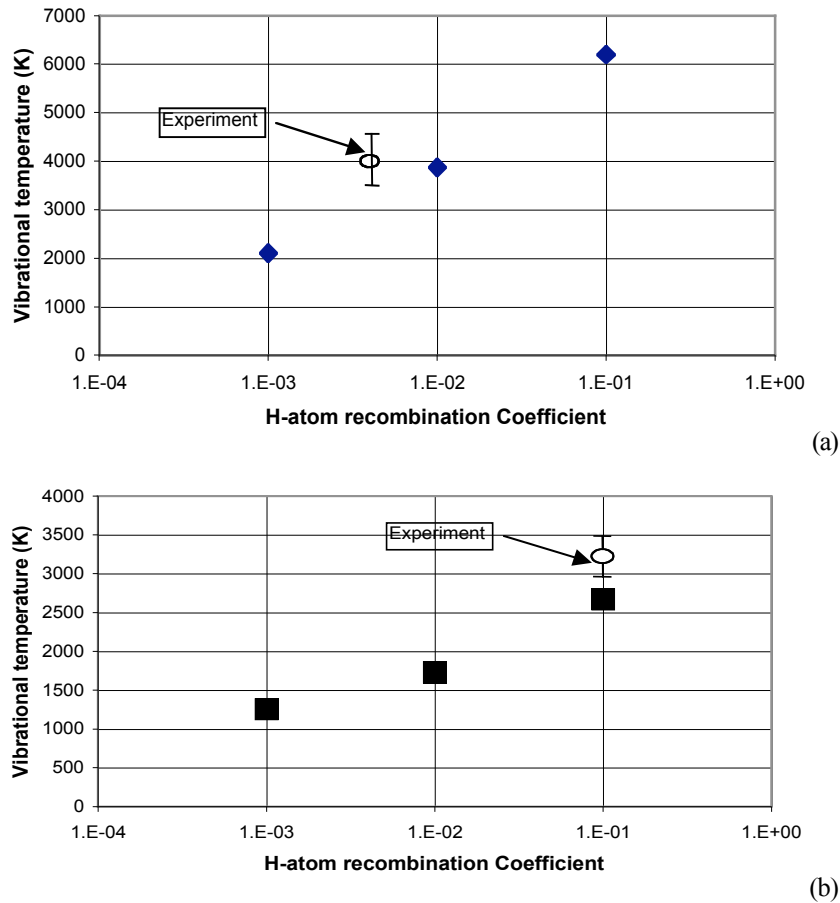
$$E_{rms} = \left( MWPD \frac{m_e}{n_e e^2} \right)^{1/2} \left( \int_{\varepsilon} \frac{v}{v^2 + \omega^2} f(\varepsilon) d\varepsilon \right)^{1/2} \quad (10)$$

where  $\omega$  is the angular frequency of the RF field,  $m_e$ ,  $e$ ,  $n_e$ ,  $\epsilon$  and  $f(\epsilon)$  are the mass, the charge, the density, the energy and the distribution function of electrons,  $\nu(\epsilon)$  is the electron-heavy particle collision frequency.

The model includes a total energy equation that yields the gas temperature that governs the rate constants of the collisions that involve heavy species and a quasi-homogeneous plasma transport model for the estimation of species and energy losses at the plasma reactor wall.

The coupling between all the sub-models is realized through a detailed radiative and collisional model<sup>30</sup>.

We analyzed and interpreted vibrational and experimental temperatures of molecular hydrogen obtained by Coherent Anti-Stokes Raman Spectroscopy (CARS) in radiofrequency inductive plasmas in the following discharge conditions: (a) pressure=1torr, injected power=0.5W, plasma length=27cm, radius=1.27cm, wall temperature=370K; (b) pressure=6torr, injected power=2.0W, plasma length=27cm, radius=1.27cm, wall temperature=550K. We report comparisons between theoretical and experimental vibrational temperatures defined on the basis of the  $v=1$  level to  $v=0$  level population ratio as a function of the recombination factor (Fig. 3). Theoretical vibrational temperatures increase with the increase of  $\gamma_H$ .



**Fig. 3. Theoretical vibrational temperature as a function of the atom recombination coefficient. (a) pressure=1torr, injected power=0.5W, wall temperature=370K; (b) pressure=6torr, injected power=2.0W, wall temperature=550K.**

The difference in the  $\gamma_H$  values can be partially explained by the different experimental wall temperatures. The variation of the recombination factor reflects obviously on the other features of an RF discharge. In particular increasing  $\gamma_H$  leads to the increase of both the

vibrational temperature and the density associated with the plateau of the vibrational distribution (Fig. 4).

On the other hand the increase of  $\gamma_H$  results in warming up the EEDF (Fig. 5) with a subsequent increase of the electron temperature (Fig. 6).

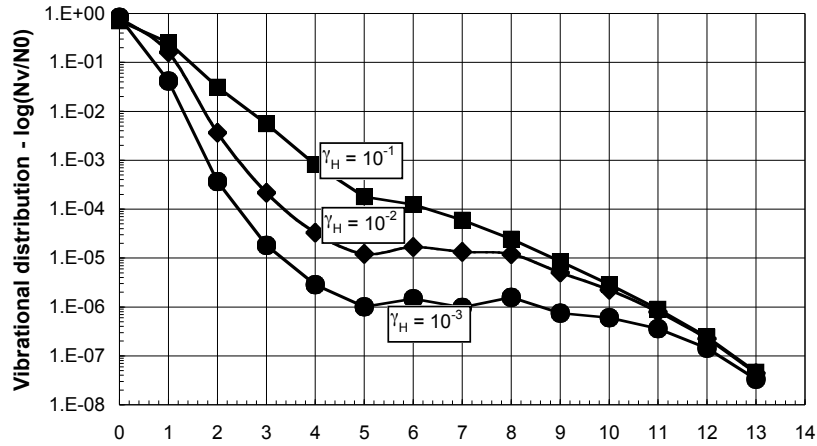


Fig. 4. Vibrational distribution functions for different  $\gamma_H$  values.

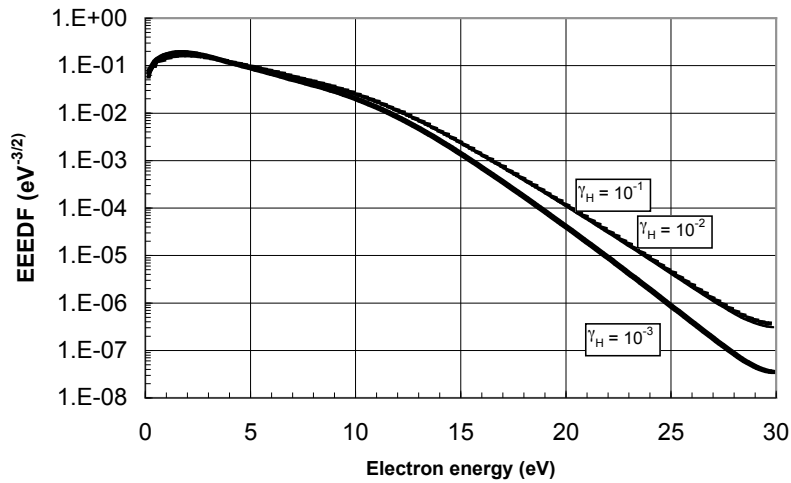


Fig. 5. Electron energy distribution function for different  $\gamma_H$  values.

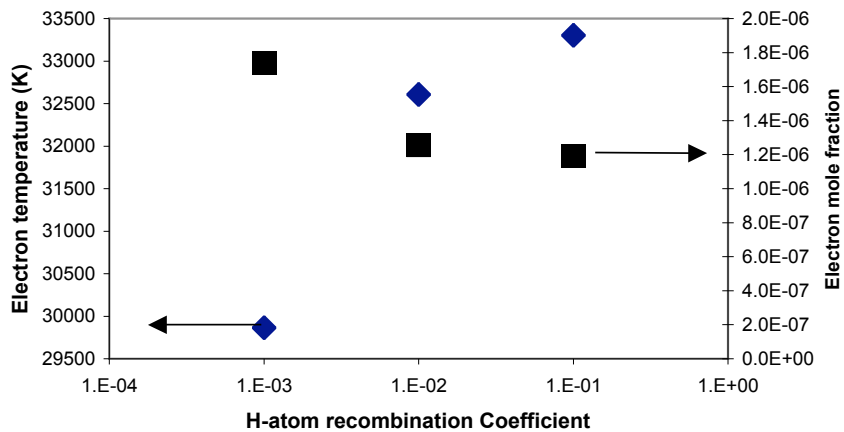


Fig. 6. Total electron density and electron temperature as a function of  $\gamma_H$ .



### 1D(r)2D(v) PIC/MCC Model of RF Parallel Plate Discharges

A 1D(r)2D(v) fully self-consistent particle/continuum model has been developed to study capacitively coupled RF discharge plasmas in hydrogen<sup>37</sup>. The code includes a state-to-state reaction diffusion model.

Also in this case it is necessary to realize a self-consistent coupling of the electron transport with the chemical kinetics, i.e. to solve at the same time the electron transport and chemical kinetics problems taking into account their reciprocal connection.

During the calculations, the densities of different species will be updated by solving appropriate equations. The approach is different for charged and neutral particles.

To solve the problem we use a Particle in Cell/Monte Carlo method for the transport equation and a grid-discretized relaxation technique for the reaction-diffusion part. In the PIC/MCC, applied to electrons and four ionic species ( $H_3^+$ ,  $H_2^+$ ,  $H^+$  and  $H^-$ ), the Newton equation for a large ensemble of mathematical point particles is solved taking into account the local electric field as it results from local interpolation within a cell of a mathematical mesh.

The problem can be formalized as follows:

$$\left( \frac{\partial}{\partial t} + v_x \frac{\partial}{\partial x} - \frac{q_s}{m_s} \frac{\partial \varphi(x,t)}{\partial x} \frac{\partial}{\partial v_x} \right) f_s(x, \mathbf{v}, t) = C_s(\{F_c\}) \quad (11)$$

$$\frac{\partial^2 \varphi(x,t)}{\partial x^2} = -\frac{1}{\epsilon_0} \sum_s q_s \int d^3 v f_s(x, \mathbf{v}, t) \quad (12)$$

$$-D_c \frac{\partial^2 n_c(x)}{\partial x^2} = \sum_r (v'_{rc} - v_{rc}) k_r \langle \{f_e\}_i \rangle \prod_{c'} n_{c'}^{v_{rc}} \quad (13)$$

where  $f_s$  and  $F_c$  are the kinetic distribution functions for the  $s$ -th charged species and the  $c$ -th neutral species respectively,  $q_s$  and  $m_s$  are the  $s$ -th species electric charge and mass,  $\varphi$  is the electric potential,  $n_c$  is the number density of the  $c$ -th neutral component,  $D_c$  is its diffusion coefficient,  $k$  and  $v$  are, respectively, the rate coefficient and the molecularity of the  $c$ -th species in the  $r$ -th elementary process.

In eq. (11)  $C_s$  is the Boltzmann collision integral for charged/neutral particle collisions:

$$C_s(\{F_c\}) = -f_s(v) \int d^3 v' p_{v \rightarrow v'} + \int d^3 v' p_{v' \rightarrow v} f_s(v') \quad (14)$$

$$p_{v' \rightarrow v} = \int d^3 w d^3 w' |v' - w'| \sum_k \sigma_k(v', w', v, w) F_{c(k)}(r, w')$$

where  $k$  is an index addressing a specific collision process,  $\sigma_k$  and  $c(k)$  are the differential cross section and the neutral collision partner of the  $k$ -th process.

The PIC method delivers a solution of the Vlasov-Poisson plasma problem in the following form

$$f_s(\mathbf{r}, \mathbf{v}, t) = \frac{W_s}{N_s} \sum_{p=1}^N S(\mathbf{r} - \mathbf{r}_p) \delta(\mathbf{v} - \mathbf{v}_p) \quad (15)$$

$W_s$  is the ratio between real and simulated particles and  $S$  is the particle shape factor which describes the way particles are assigned to the mesh.

The density for the neutral species are obtained by finding a stationary solution for the a set of non-linear equations equal to that given in equation (1) except for a diffusion term that in one dimension reads as:

$$\left( \frac{dN_v}{dt} \right)_{diffus} = D_v \frac{\partial^2 N_v}{\partial x^2} \quad (16)$$

After any calculation step of the motion equations, the electric charge in any cell of the mesh is determined from the number of electrons and ions found in the cell itself, according to

their statistical weight. Known the electric charge density, the electric potential and field are determined by solving the Poisson equation on the mesh.

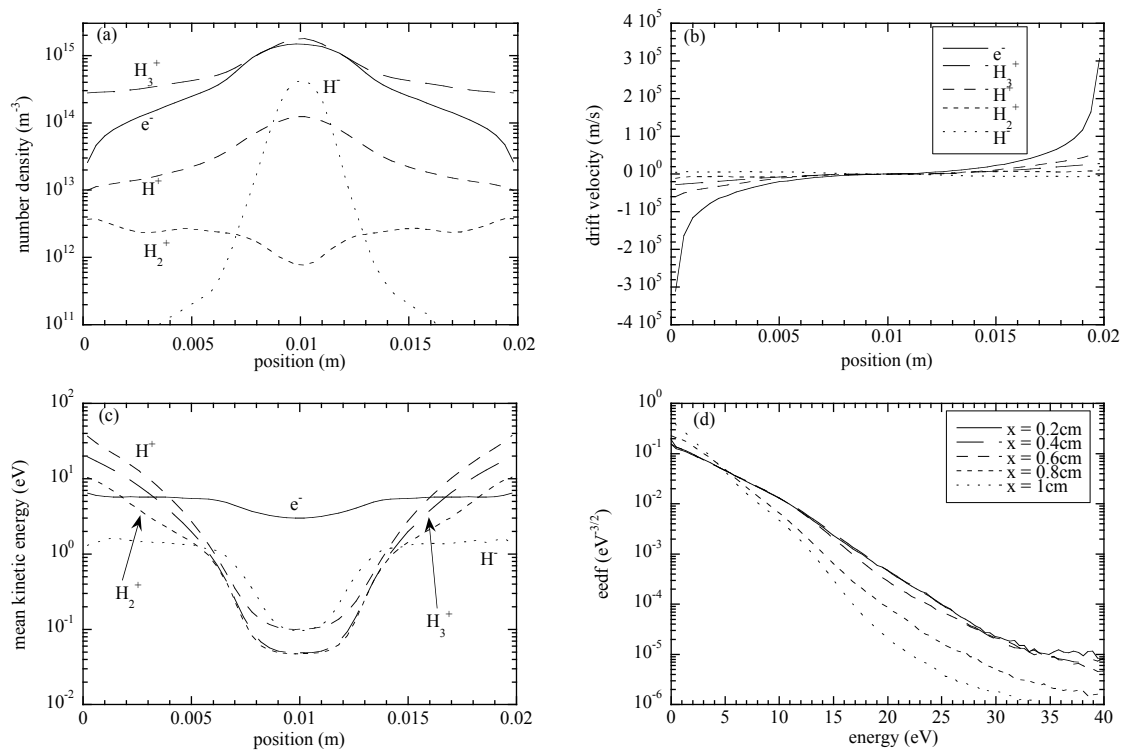
The electron-molecule process rates are calculated as a function of the position taking into account the translational non equilibrium of electrons and the vibrational non equilibrium of molecules.

As regard the inclusion of the Boltzmann collision term  $C_s$ , as it has been demonstrated<sup>43</sup>, a stochastic calculation of  $C_s$  in the von Neumann sense delivers directly an improved version of the null-collision Monte Carlo method including the thermal distribution of neutrals.

Recombination processes cannot fit the basic PIC/MCC formalism since they involve two charged particles. These processes are treated as a combination of two first order ones, each including one of the two particle species involved in the process.

The model has been applied to a discharge in pure hydrogen, produced by into a parallel-plate high frequency reactor. One of the plates ( $x=0$ ) (the so-called “grounded electrode”) is constantly kept at zero voltage, while the other one (the “powered electrode”) is assumed to be driven by an external generator to an oscillating voltage.

We present some results calculated considering the following physical conditions: gas temperature=300K, voltage amplitude=300V, gas pressure=1torr, discharge frequency=13.56MHz, discharge gap=0.02m, DC voltage (bias)=0V.

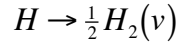


**Fig. 7. Plasma phase quantities in typical conditions for the probability parameters ( $\gamma_v=0.05$ ,  $\gamma_H=0.2$ ): (a) number density, (b) drift velocity, (c) mean kinetic energy of charged species as a function of position and (d) EEDF as a function of energy.**

In Fig. 7 plasma phase quantities in typical conditions for the probability parameters ( $\gamma_v=0.05$ ,  $\gamma_H=0.2$ ) are shown. In particular: (a) number density, (b) drift velocity, (c) mean kinetic energy of charged species as a function of position and (d) electron energy distribution function as a function of energy. From (a) it is evident a slight electronegative behaviour in the centre of the discharge as shown by the separation of the positive ion and electron density in the bulk plasma. The EEDF as shown in (d) significantly deviates from the Maxwell-

Boltzmann law showing the necessity of including a kinetic level description of the electron transport.

Table 1 reports the results obtained for  $H^-$  ions, H atom and electron density varying the vibrational level on which H atoms recombine at the reactor walls, according to the reaction



It can be noticed that the level of recombination has a significant effect on  $H^-$  density, while the other quantities are not considerably affected.

**Table 1. Influence of the vibrational level for H-atom wall recombination.**

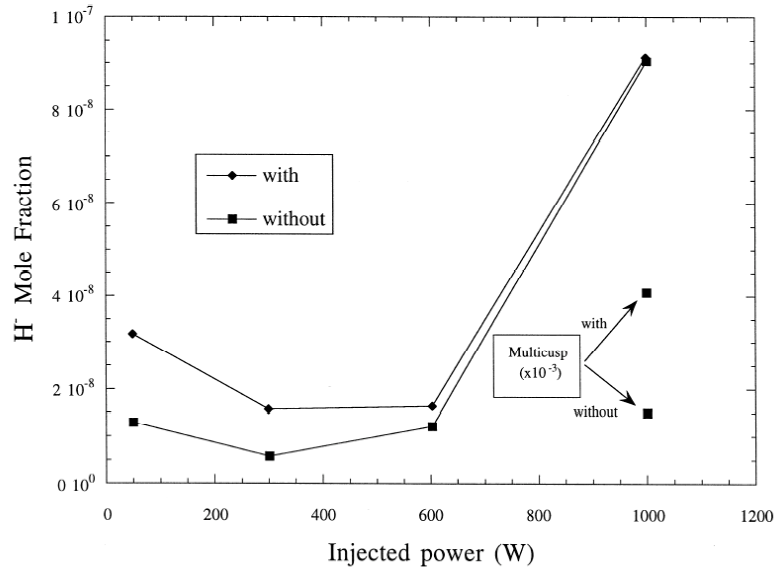
	$n_{H^-} / m^{-3}$	$n_H / m^{-3}$	$n_e / m^{-3}$
$v = 0$	$3 \times 10^{14}$	$7.3 \times 10^{18}$	$1.15 \times 10^{15}$
$v = 7$	$5.72 \times 10^{14}$	$7.4 \times 10^{18}$	$1.18 \times 10^{15}$
$v = 14$	$6 \times 10^{14}$	$7.4 \times 10^{18}$	$1.18 \times 10^{15}$

## Conclusions

In conclusion we can say that vibrational kinetics in  $H_2$  plasmas is a subject in continuous evolution having a strong impact in different pure and applied research fields. In particular the future ITER project will use negative ion sources for heating the tokamak. This point is generating a renewing interest in the vibrational kinetics of  $H_2/D_2$  plasmas as can be appreciated by the large european activity in the field by fusion and cold plasma communities.

We presented different approaches to study vibrational kinetics coupled to electron one for modelling different kinds of negative ion sources. In particular we improved the numerous input data describing the negative ion production in multipole, microwave and parallel plate reactors.

However, a complete understanding of the production mechanism of negative ions should require also the inclusion in the model of Rydberg excited states of atomic hydrogen, as it has been shown by Hassouni *et al.*<sup>18</sup>.



**Fig. 8.  $H^-$  concentration as a function of the injected power calculated including (with) and neglecting (without) dissociative attachment from Rydberg states<sup>18</sup>.**

Moreover, the role of alkaline metals atoms (such as Cs) in enhancing the negative ions production will be investigated.

## Acknowledgement

This work has been partially supported by ASI (I/R/055/02) and MIUR (cof.2003 Project No. 2003037912\_010).

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