From cold to fusion plasmas: spectroscopy, molecular dynamics and kinetic considerations
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Abstract. Non-equilibrium effects in hydrogen plasmas have been investigated in different systems, ranging from RF plasmas to corona discharges. Existing measurements of vibrational and rotational temperatures, obtained by different spectroscopical techniques are reported, rationalized by results calculated by kinetic models. Input data of these models are discussed with particular attention on the dependence of relevant cross sections on the vibrational quantum number. Moreover the influence of vibrational excitation of the H$_2$ molecules in affecting the translational distribution of atoms in ground and excited levels is shown. Finally a collisional radiative model for atomic hydrogen levels, based on the coupling of the Boltzmann equation for EEDF and the excited state kinetics, is presented, emphasizing the limits of quasi–stationary approximation. In this last case, large deviations of the EEDF and atomic level distributions from the equilibrium are observed.
1. Introduction

Fusion plasmas are characterized by very high temperatures that, while preventing the existence of neutral species, still allows multi-charged radiating species. This radiation, coming from impurities generated by wall erosion or added by ad-hoc injection, can be used to get information about the electron temperature. In these last years however “cold plasmas” are becoming very popular in the fusion community because they determine the properties near the divertor where a moderate electron density and temperature exist. Under these conditions the vibrational manifold of the molecular species is well populated having strong consequences on the behaviour of the whole system. On the other hand, vibrationally excited molecules of \( \text{D}_2 \) and \( \text{H}_2 \) species play a paramount role in creating negative ion sources to be used as neutral heating in the ITER project [1]. Plasma conditions in the negative ion sources (NIS) are not so far from those met in the divertor region (DR) so that spectroscopic and kinetic methods studied in NIS can be extended to understand DR properties. We refer in particular to the spectroscopic methods to measure vibrational temperature and vibrational distribution function (VDF) as well as the complex kinetic models used to rationalize these measurements [2, 3]. Non equilibrium vibrational distributions are controlled not only by electron molecule impact collisions i.e. the so called e–V and E–V pumping processes [1, 2, 3] but also by quenching processes involving atomic species, in particular the process

\[ \text{H} + \text{H}_2(\nu, j) \leftrightarrow \text{H} + \text{H}_2(\nu', j') \]

In turn the reaction rates of this process demands the knowledge of the translational temperature \( T_g \) of atomic hydrogen (deuterium), which in general is much higher than the corresponding one for molecular species. This indicates the importance of the atomic neutral temperature in determining the form of VDF. Theoretical and experimental line widths of atomic H can be used to get information on \( T_g \), being the line broadening controlled by electron atom collisions [4] and electron dissociative-excitation processes [5, 6, 7].

Atomic emission spectroscopy is still largely used to get information about the electronic distribution of excited states yielding information on the electron temperature. Also in this case one should accompany the spectroscopic measurements with suitable collisional radiative (CR) models which take into account collisions of free electrons with atoms and molecules [8, 9]. It should be noted that under many situations the electron energy distribution function (EEDF) can deviate from the Maxwell one implying the necessity of solving an appropriate Boltzmann equation for EEDF [1, 2, 8]. These considerations clearly reaffirm the strong linking between spectroscopic measurements and atomic and molecular physics, the last important for the construction of kinetic models used to deconvolute the experimental observations. The aim of this paper is indeed to present some study-cases which can emphasize this linking with particular attention on the importance of vibrationally excited molecules.

The paper is divided into different sections. Section 2 deals with the measurement of vibrational and rotational temperatures by CARS (Coherent AntiStokes Raman Spectroscopy) and by Vacuum Ultra Violet (VUV) absorption spectroscopy, as well as the kinetic models used to razionalize the experimental results. Section 3 reports emission involving Fulcher system in different plasma conditions (hollow-chatode discharges and parallel plate RF reactors). Section 4 reports the influence of vibrational excitation on the translational distribution functions of atomic hydrogen.
and protons. Section 5 shows results of a collisional radiative model, obtained by coupling the kinetics of excited states and Boltzmann equation for EEDF.

2. CARS spectroscopy

CARS spectroscopy is probably the most used method for getting information on vibrational and rotational temperatures of \( \text{H}_2 \), \( \text{D}_2 \) plasmas under different conditions including DC discharges [10, 11], multipole magnetic [12] and RF plasmas [13, 14]. In this paper we report a sample of results recently obtained by our group under RF inductive plasma conditions [13, 14] as well as the theoretical model used for rationalizing the results.

The experimental set-up included the RF inductive discharge plasma reactor and vacuum chamber for CARS technique calibration, a system for gas feeding and pumping out, a pressure controlling system, the CARS system with optics to recombine and focus the pump laser beams for generating the CARS spectrum, an automatic system for data acquisition and processing [14]. The longitudinal, tube-type, RF configuration (diameter 3.2 cm and 54 cm length) was designed to achieve large concentrations of vibrationally excited \( \text{H}_2 \). Up to 5 kW of the RF power supply operating at 27 MHz was used to inductively couple the RF power into the plasma through an impedance-matching network and a multiple-turn, water-cooled copper work coil (80 mm in length and 50 mm in inner diameter). Figure 1 shows average values of the rotational temperature, \( T_{\text{rot}} \), and vibrational temperature, \( T_{1 \rightarrow 0} \), as function of the total pressure in the RF inductive discharge plasma in the molecular hydrogen for various power releases. The experimental data were evaluated from the CARS spectra processing, as illustrated in [14]. These CARS spectra were taken from the probe volume positioned on the axis and in the central zone of the RF inductive coil.

![Figure 1](image-url)

**Figure 1.** Experimental vibrational and rotational temperatures of the \( \text{H}_2 \) ground electronic state \( (X^1\Sigma_g^+) \) as a function of pressure, in RF inductive discharge plasma [14].

Inspection of figure 1 shows that the average values of the vibrational temperature decreases monotonically from 4 300 K to 2 800 K by increasing the total pressure from
Table 1. Calculated $T_{vib}$ for different $\gamma_H$ values compared with experimental values for case (a) and case (b) RF plasma conditions.

<table>
<thead>
<tr>
<th>$T_{vib}(\gamma_H=10^{-3})$</th>
<th>$T_{vib}(\gamma_H=10^{-2})$</th>
<th>$T_{vib}(\gamma_H=10^{-1})$</th>
<th>$T_{exp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>case (a)</td>
<td>case (b)</td>
<td>2000</td>
<td>3900</td>
</tr>
<tr>
<td>1250</td>
<td>1700</td>
<td>2700</td>
<td>3200±250</td>
</tr>
</tbody>
</table>

66.6 to 1066.6 Pa (power input from 0.5 to 2 W/cm$^3$). At the same time average values of the rotational temperature increase with the pressure from 560 to 750 K.

At the low rotational levels $J=0-5$, the relaxation rates between the rotational and translational degree of freedom of the hydrogen molecules are very high so that the measured rotational temperature $T_{rot}$, can be considered equal to the gas temperature in the investigated range of the total pressure.

A detailed kinetic model describing RF plasmas has been discussed in [13].

Basically the model includes:

- a non equilibrium vibrational kinetics sub-model to describe the vibrational distribution function (VDF) of H$_2$ molecules ($\nu=0$-14) and the dissociation through the vibrational pumping mechanism;
- a collisional radiative model describing the kinetics of electronically excited states of both atomic and molecular hydrogen;
- a collisional model that describes the dissociation, attachment and ionization kinetics, ion conversion and recombination processes and mutual neutralization of negative and positive ions;
- a sub-model of the electron kinetics that enables to determine the electron energy distribution function (EEDF) required to estimate the rate constants for electron-heavy species collisions;
- a total energy equation that yields the gas temperature that govern the rate constants of the collisions that involve heavy species;
- a quasi-homogeneous plasma transport model for the estimate of species and energy losses at the plasma surrounding wall.

The model has been in particular used to reproduce the experimental data for the two following discharge conditions:

(a) pressure = 133.3 Pa; injected power density = 0.5 W cm$^{-3}$; plasma length $\sim$ 27 cm; radius = 1.27 cm; wall temperature = 370 K
(b) pressure = 800 Pa; injected power density = 2 W cm$^{-3}$; plasma length $\sim$ 10 cm; radius = 1.27 cm; wall temperature = 550 K.

Table 1 reports a comparison between theoretical and experimental vibrational temperatures for cases (a) and (b).

The theoretical values have been calculated by different $\gamma_H$ values (taken as a parameter) i.e. by different values of the heterogeneous recombination coefficient of the process

$$2H + W \leftrightarrow H_2 + W$$

In both cases, the theoretical vibrational temperatures increase with the increase of $\gamma_H$, due to the corresponding decrease of the concentration of atomic hydrogen in gas conditions.
phase which play a fundamental role in deactivating vibrationally excited molecules. It should be noted that a satisfactory agreement between theoretical and experimental vibrational temperatures is reached for $\gamma_H=10^{-2}$ for case (a), while a recombination factor of the order of $10^{-1}$ is needed to reproduce the vibrational temperature at high pressure (case (b)). The difference in the recombination coefficient values can be at least partially explained by the dependence of $\gamma_H$ on wall temperature. The theoretical model developed in [13] is also able to describe the whole VDF and EEDF, not accessible by experiments. Figure 2 a and b report VDF and EEDF, for case (a) and for different values of $\gamma_H$, respectively. Inspection of the two figures show large deviations of the two distributions from the corresponding Boltzmann and Maxwell ones, which should appear as straight lines in the two plots. The strong dependence of distributions on $\gamma_H$ is again due to the change in the composition of the mixture of the molecular and atomic components (see [13] for details).

Figure 2. VDF (a) and EEDF (b), for case (a), for different $\gamma_H$ values [13].

CARS spectroscopy while being essential to measure the vibrational and rotational temperatures of H$_2$ and D$_2$ can be hardly applied for measuring high vibrational levels ($\nu > 4$), molecules which play a role of paramount importance in the formation of negative H$^-$/D$^-$ ions through dissociative attachment. To this end many techniques have been used including multi-photon ionization [15], resonant enhanced dissociative attachment [16] and VUV (vacuum ultraviolet) absorption [17]. The listed techniques have been in particular used for measuring H$_2$ non-equilibrium vibrational distributions in magnetic multipole discharges. These discharges operate at low pressure ($\sim 0.1$ Pa) and are formed by electrons emitted by filaments and accelerated by applied voltages ($\sim 100$ V). The electrons form a plasma characterized by vibrational and electron energy distributions that markedly differ from the Boltzmann and Maxwell ones. Large deviations of EEDF from the Maxwell behavior is in fact observed as can be seen from figure 3. A quasi-bi-maxwellian EEDF is found, due to the continuous inlet of high energy electrons (90 eV) in the reported case and to the subsequent thermalization of part of this electrons due to inelastic, superelastic and elastic collisions (see [18] for details).

Moreover a large plateaux in VDF can exist in these discharges as a result of the so called E-V mechanism i.e. excitation of singlet states of H$_2$, D$_2$ and subsequent optical decay in the ground electronic state. A lot of theoretical models have been
used to rationalize the experimental VDF, essentially based on the coupled solution of the vibrational and electron kinetics, similar to the previous model [18]. The satisfactory agreement between experimental (VUV absorption) and theoretical results (see figures 4 a and b) is a further indication of the possibility of using theoretical and experimental methodologies developed for cold plasma to fusion ones, a point being emphasized by fusion researchers [19, 20].

**Figure 3.** Stationary EEDF for different discharge currents, for \( p=1.5 \) Pa and \( V_d=100 \) V [18].

**Figure 4.** \( \text{H}_2 \) VDF for different values of the discharge current ((a) \( I_d=0.5 \) A (b) \( I_d=10 \) A), at pressure \( p=1.5 \) Pa and discharge voltage \( V_d=100 \) V, (circles) experimental results [17] (squares) theoretical results [18].
3. Fulcher-α Band: a diagnostic tool

3.1. Hollow-cathode glow discharge

The Fulcher-α band spectroscopy represents a valuable tool for the indirect experimental determination of the vibrational and rotational distributions of the H$_2$ ground electronic state, widely used under different plasma conditions spanning from coronal discharge to the diagnostic of the divertor region in controlled fusion experiments. The emission spectrum of the excited ro-vibrational levels of the d$^3\Pi_u$ state ($n=3$) radiatively decaying to the ro-vibrational of the a$^3\Sigma^+_g$ state ($n=2$) is, in fact, conveniently located in the visible region and is characterized by a relatively high intensity. The usable lines are actually limited to the transitions allowed according to the ro-vibronic sub-level selection rules, usually selecting the Q branch originating from d$^3\Pi_u^-$ term ($\Delta J=0$) due to the anomalous intensity of the spectrum for P and R branches from d$^3\Pi_u^+$ ($\Delta J=\pm1$) [21, 22, 23], and also considering those transitions initiated from the lowest vibrational levels ($\nu'<4$), due the observed efficient predissociation depleting the higher levels [24].

The derivation of the VDF in the X$^1\Sigma^+_g$ state, in the frame of a “coronal model” for low-density plasmas, relies on some theoretical assumptions:

- ground state VDF is Boltzmann, characterized by the temperature $T_{vib}$
- the d$^3\Pi_u$ state is populated by excitation of ground state hydrogen molecules in collision with electrons
- the population of the considered emitting levels is negligibly affected by predissociative and collisional quenching processes

![Figure 5](image.png)

**Figure 5.** Experimental vibrational and rotational temperatures of the H$_2$ ground electronic state (X$^1\Sigma^+_g$) as a function of pressure, in hollow-cathode glow plasma, obtained from the intensity of the Fulcher-α band spectra, by a coronal model [25].

In figure 5 the rotational and vibrational temperatures of the ground H$_2$ molecule, measured in a hollow-cathode glow discharge apparatus, are reported in a wide
pressure range, thus showing the weak dependence of these quantities on the neutral density \[25\].

However caution should be used in the analysis of the results, obtained in the hypothesis of a VDF in the ground state perfectly mirrored by the vibrational distribution of the emitting excited state. Typical electron density values in divertor region, \(n_e \approx 10^{14} \text{ cm}^{-3}\), are considerably higher than in technical plasmas and the theoretical model must describe the interplay of different elementary processes, thus considering the different vibrational pumping/de-activation mechanisms of excited electronic states. Attempts in this direction are reported in literature \[26\], improving the collisional radiative model by Sawada&Fujumoto \[27\] for hydrogen molecules and atoms. Results \[26\] clearly indicate that while at low electron densities the pumping mechanism of the excited emitting state is dominated by the forbidden electron-impact induced excitation of the ground state, increasing \(n_e (> 10^{12} \text{ cm}^{-3})\) the excitation is governed by transitions involving metastable excited states \(\alpha^{3}\Sigma^+_g, \epsilon^{3}\Pi_u\), with intermediate regimes where both mechanisms are important in populating the emitting state \[28\].

These considerations justify the efforts done in the dynamical investigation on the probability of electron-H\(_2\) collision processes initiated from electronically excited states, with particular attention to the allowed transitions \(n = 2 \rightarrow n' = 3\) between triplet terms \[29\], in the perspective of a more sophisticated molecular radiative model fully-resolved in the electronic degree of freedom. As in the case of the ground-state excitation, the role of vibration in enhancing the probability of these excited-state–excited-state transitions should be investigated. In this context the dependence on the both initial and final vibrational quantum numbers of cross sections for the process

\[
e + H_2(\alpha^{3}\Sigma^+_g, \nu) \rightarrow e + H_2(\epsilon^{3}\Pi_u, \nu')
\]

are reported in figure 6. Results, obtained within the semi–classical impact parameter method, explore the whole domain of variability of \(\nu\), while selected \(\nu'\) values are considered, corresponding to the levels that, not undergoing predissociation, could contribute to the emission radiating back to the \(\alpha^{3}\Sigma^+_g\) state. The relative position of the corresponding potential energy curves strongly favour the vibrational wavefunction overlap, accounting for a dominant role of diagonal state-to-state transitions, i.e. \((\nu = \nu')\), and negligible direct dissociation.

In figure 7 the excitation cross sections for the forbidden transition \(X^{1}\Sigma^+_g \rightarrow \epsilon^{3}\Pi_u\), calculated in the Born-Rudge approximation, have been displayed, for selected vibrational levels of the ground state. For the \(\nu=0\) case also the partial excitation cross section resulting from the summation over the first four vibrational levels, actually contributing to the emission, is reported. The results for \(\nu=0\) are in satisfactory agreement with the available experimental \[30\] and theoretical \[31\] data available in literature. The vibrational excitation of the target is effective only in the near threshold region, where also the peak is located, while for higher values of collision energy the process is even less favored increasing the initial vibrational quantum number.
Figure 6. State-to-state cross section for electron-impact induced excitation of selected final vibrational levels $\nu'$ of $d^3\Pi_u$ state of H$_2$ molecule, as a function of collision energy for different initial vibrational levels, $\nu$, of the $a^3\Sigma^+_g$ state. (a) $\nu'=0$; (b) $\nu'=1$; (c) $\nu'=2$; (d) $\nu'=3$.

Figure 7. Excitation cross section for electron-impact induced excitation of $d^3\Pi_u$ state of H$_2$ molecule, as a function of collision energy for different initial vibrational levels, $\nu$, of the $X^1\Sigma^+_g$ state (dotted line curve represents the integral cross section obtained summing up to $\nu'=3$). A comparison with theoretical [31] (long-dashed line) and experimental [30] (close markers) results for $\nu=0$ level.
3.2. Parallel plate RF discharges in H$_2$

In view of their importance in the context of material processing (e.g. diamond films, silicon films) and electronic manufacturing (e.g. deposition of low-k dielectrics), the electric discharge plasmas generated in hydrogen-rich gas mixtures have attracted much attention. In particular, measurements have been performed on capacitively coupled discharges in pure hydrogen and hydrogen diluted methane, reporting the emission intensity of the Balmer-alpha and Fulcher lines resolved in space and time [32, 33, 34, 35]. A remarkable feature of the space profile of the intensity is a double maximum observed in particular close to the electrodes at the higher values of the discharge power. In [33] an interpretation of this feature was provided, in terms of a double layer dynamics of the sheath field, but a theoretical model was still not possible, except for a determination of ionization rate determined by simplified fluid (macroscopic) and particle-in-cell Monte Carlo (PIC-MC, kinetic) calculations. The use of kinetic models is highly valuable for these studies since they allow to take into account the space and time dependence of the eedf and its connection to the sheath dynamics through the generation and transport and charged species. Fluid models, instead, are based on a macroscopic description of the charged particle kinetics in the discharge. These models assume for the ionization coefficient, and in general for the rate coefficients of the electron/molecule reactions, values which are at most calculated by solving the so-called quasi-isotropic Boltzmann equation assuming a uniform plasma. These are later interpolated in terms of the electron energy and applied locally depending on the calculated value of the electron temperature. Fluid models are much less computationally expensive but usually give inaccurate results at the lower pressure values. In [34] additional experimental results were provided to support an interpretation of the feature as due to collision induced ion drag leading to sheath collapse, coherently with the absence of the feature in atomic gas under similar conditions. In [35] a connection was established between the profiles of the emission intensity and those of the electric field, providing a much convincing support to the sheath dynamic interpretation on an experimental basis. However, only in [36], for the first time, a theoretical calculation of the excitation rates of H($n=3$) and H$_2$(d$^3$Π$_u$), respectively, was reported for different discharge voltages using a hybrid model, including a PIC-MC calculation of charged species dynamics (e, H$^+$, H$_2^+$, H$_3^+$, H$^-$) and a reaction-diffusion calculation of the VDF of H$_2$(X$^1$Σ$_g^+$,$\nu$). Due to the low radiative lifetimes of the emitting states it was supposed that the population rate of these last is proportional to the emission intensity for both lines. A qualitative agreement was found, with a reproduction of the double maxima of the space emission profile of both lines and a semi-quantitative agreement concerning the location of these features, which was found to depend weakly on the discharge voltage when this last was high enough to allow the feature to appear. We show for the first time results based on an updated version of the model in [36]. The improvements concern the possibility to deliver space-time plots of the population rates and the inclusion of a more consistent set of cross sections for the Balmer-α emission via H$_2$(X$^1$Σ$_g^+$,$\nu$) dissociation to H($n=3$), based on the latest results in [37, 38].

Cross sections for the process of electron-impact induced direct dissociation through the repulsive branch of two bound states, D$^1$Π$_u$ and B$^0$′$^1$Σ$_u^+$, both correlating to the correlating with H(1s)+H$^*$($n=3$) dissociation limit, were obtained in the frame of the semi-classical impact parameter method, with resolution on the initial vibrational quantum number, $\nu$. The vibrational excitation of the molecular target
acts enhancing the process probability, showing the dependence on \( \nu \) a strongly irregular behavior that follows closely the behavior of corresponding Franck-Condon density.

![Diagram](attachment:image.png)

**Figure 8.** Cross section for electron-impact induced direct dissociation of \( \text{H}_2 \) molecules through excited singlet states as a function of collision energy for different initial vibrational levels. (a) state \( B''^1\Sigma_u^+ \) (b) state \( D^1\Pi_u \).

In figures 9 a and b we report results for the excitation rate of \( \text{H}_2(d^3\Pi_u) \) as a function of space and RF phase in the same conditions in [36] at two different voltages. In these figures the time is measured in terms of phase with respect to the RF oscillation at 13.56 MHz: the population rate increases when the sheath dynamics heats up the free electron cloud and increases the value of the eedf beyond the process threshold. The figures show the contribution of the expanding sheath (the two maxima closer to the discharge center) as well that of the collapsing sheath (closer to the electrodes), qualitatively coherent with experimental results [32, 33, 34]. The effect of voltage is manifest since at lower voltage the contribution of sheath collapse to excitation rate becomes negligible.

![Diagram](attachment:image.png)

**Figure 9.** Excitation rate \([\text{cm}^{-3}\text{s}^{-1}]\) for the \( \text{H}_2(d^3\Pi_u) \) as a function of space and RF phase for a discharge with the following parameters: \( p=66.6 \text{ Pa}, \nu_{RF}=13.56 \text{ MHz}, d=3 \text{ cm} \) for two different RF voltages: (a) 447 V and (b) 145 V.

In figure 10 we show the time averaged, space dependent excitation rate of \( \text{H}(n=3) \) as results from the sum of two channels (via \( D^1\Pi_u \) and \( B''^1\Sigma_u^+ \) states) showing
the detailed contribution of the vibrational states of H$_2$(X$^1\Sigma^+_g$). In the figure it is possible to appreciate the space dependence of the different contributions. Note that only half of the space domain is considered because of the symmetry of the plasma conditions. As expected, since the voltage is high enough to show the double layer, a double maximum is observed for all rates in the sheath region since these processes are characterized by a high threshold. In this case, which is a typical operating condition for a low pressure discharge in H$_2$, the VDF is characterized by a low vibrational temperature for the 0-1 levels ($T_{0\rightarrow1}$) due to the low electron number density ($\sim 10^9$ cm$^{-3}$) and with a plateau for intermediate levels in the range 4-8 due to the antagonism of $e$+H$_2$ EV processes [39] and H$_2$+H VT processes. These features are reflected by the rate trends with $\nu$ since the cross section increasing with $\nu$ is modest, and as a consequence most of the atoms come from ground level H$_2$ molecules. In different systems, like inductive discharges or high pressure discharges, where the $T_{0\rightarrow1}$ is usually considerably higher we expect that the consideration of the EEDF and the vibrational state-to-state determination of the dissociation rate will be a neccessity to get an accurate result. These results illustrate the power of state of the art modeling applied to these technologically important systems.

![Figure 10.](image)

**Figure 10.** Time averaged excitation rate for the H(n=3) as a function of the axial position in the discharge and the vibrational quantum number of the H$_2$(X$^1\Sigma^+_g$, $\nu$) state in the same conditions of figure 9 a.
4. Translational energy distribution functions of atomic hydrogen and protons

The vibrational excitation of molecular target acts, in general, enhancing direct dissociation and ionization processes, thus affecting the population of electronically excited H atoms and, in turn, the intensity of atomic emission lines. Modeling of non equilibrium vibrational distributions requires state-to-state cross sections resolved on the vibrational degree of freedom for different channels [5, 37, 38].

From the previous study cases we have underlined the role of atomic hydrogen in affecting the vibrational distribution of H\(_2\) (D\(_2\)) molecules. The corresponding relaxation rates depend on the translational temperature as can be understood by inspection of the corresponding rates reported in figure 11.

These rates have been obtained by intensive QCT (Quasi-Classical Trajectory) calculations [40] of the best available PES (Potential Energy Surface).

The translational temperature depends on the dissociation and ionization channels, yielding hydrogen atoms and ions by the processes

\[
e + \text{H}_2(X^1\Sigma_g^+, \nu) \rightarrow e + \text{H}_2^+ \rightarrow e + \text{H}(1s) + \text{H}^+(n)
\]

\[
e + \text{H}_2(X^1\Sigma_g^+, \nu) \rightarrow 2e + \text{H}_2^+(2\Sigma_g^+ + 2\Sigma_u^+) \rightarrow 2e + \text{H}(1s) + \text{H}^+
\]

The translational energy distribution functions of hydrogen atoms, \(F_H(E, \varepsilon)\), and ions, \(F_{H^+}(E, \varepsilon)\), include the effect of the microscopic collisional dynamics, through the elementary processes cross sections, \(\sigma\), weighted on the vibrational distribution of the ground state

\[
F_H(E, \varepsilon) \propto \sum_i \sum_{\nu} \frac{N_{\nu}}{N_{\text{tot}}} \left[ \sigma_{\text{exc}}^i(E, \nu \rightarrow \varepsilon) + \sigma_{\text{ion}}^i(E, \nu \rightarrow \varepsilon) \right]
\]

(1)

\[
F_{H^+}(E, \varepsilon) \propto \sum_i \sum_{\nu} \frac{N_{\nu}}{N_{\text{tot}}} \sigma_{\text{ion}}^i(E, \nu \rightarrow \varepsilon)
\]

(2)

The cross sections for the \(i\)-th channel, function of energy of the impinging electron \(E\), are resolved on the initial vibrational level and on the energy of the final vibrational...
level, belonging to the continuum, in turn related to the translation energy of atomic fragments, through the threshold energy ($\varepsilon_{tr} = \varepsilon - \varepsilon_{th}$). In figure 12 a pictorial view is given, showing how the VDF of the ground state is mirrored in dissociative excitation processes.

![Energy state diagram of singlet electronic terms for H$_2$ molecule. Pictorial view of the electron-impact induced direct dissociation through the repulsive branch of bound excited states.](image)

**Figure 12.** Energy state diagram of singlet electronic terms for H$_2$ molecule. Pictorial view of the electron-impact induced direct dissociation through the repulsive branch of bound excited states.

![Translational energy distribution function of atomic hydrogen, H(1s), formed in electron-impact induced direct dissociation through $b^3\Sigma_u^+$ state, as a function of translational energy of atoms, for different values of vibrational temperature [7].](image)

**Figure 13.** Translational energy distribution function of atomic hydrogen, H(1s), formed in electron-impact induced direct dissociation through $b^3\Sigma_u^+$ state, as a function of translational energy of atoms, for different values of vibrational temperature [7].

Tanaka et al. [7] showed the dependence of the kinetic energy distribution of H(1s) atoms, formed in the dissociation through the repulsive $b^3\Sigma_u^+$ state, the main dissociative channel, on the vibrational temperature of the ground H$_2$ state (see figure 13). At low values of $T_{vib}$ excited vibrational levels are poorly populated and the distribution is characterized by a sharp peak at $\sim 3$ eV. Increasing the vibrational temperature, corresponding to higher excited level populations, a broadening of the distribution is observed, due to the spreading of the shading area in figure 12.
More complex is the case of dissociative excitation leading to excited atomic fragments, H⁺(n). In [6, 41] the distributions of H⁺(n) arising from non-equilibrium ground VDFs have been investigated. In figures 15 the translational energy distribution functions (TEDFs) of atoms with principal quantum numbers n = 3 and 4, for two different electron density values, corresponding to non-equilibrium VDFs [42] (see figure 14), are reported [6, 41]. Results were obtained considering the cross section vibrational dependence well described by Franck-Condon density factors.

![Figure 14. Non-equilibrium vibrational distribution as a function of the vibrational quantum number for different electron densities [42].](image)

The distributions are always characterized by a bimodal shape, associated to two different groups of atoms, i.e. “cold” and “hot” atoms. The slow component is due to the dissociation occurring on the repulsive branch of bound electronic states in optically allowed transitions, in fact showing a linear increase with electron energy, while fast atoms are formed in optically forbidden excitation to purely repulsive states. Vibrational excitation, populating the VDF tail, acts reducing the translational energy separation between groups. It should be noted that some processes affecting the TEDF have been neglected in this model, such as the dissociation through the doubly excited states, leading to pairs of excited atomic fragments.

Considerations can be extended to the theoretical TEDF obtained for protons (see figure 16) [41] and are confirmed also by experiments [43].
Figure 15. Translational energy distribution function of excited atomic hydrogen, $H^*(n)$, formed in electron-impact induced direct dissociation, as a function of translational energy of atoms, at electron impact energy $E=50$ eV for different electron densities [6, 41].

Figure 16. Translational energy distribution function of proton, formed in electron-impact induced ionization, as a function of translational energy of H-H$^+$ pair, at electron impact energy $E=50$ eV for different electron densities [41].
5. Collision Radiative model of atomic hydrogen plasma

To relate the emission properties of hydrogen plasmas to non-equilibrium distributions, the CR model is solved under the quasi-stationary state approximation [44, 45] (QSS-CR). This model was applied mainly to atomic systems [44, 45, 46, 47, 48], but in some cases it has been extended to molecular plasmas [26]. The main hypothesis of QSS-CR model is that macroscopic quantities such as electron density and temperature as well as the population of the ground state, change much slower than the population of the excited states. As a consequence, the distribution of internal states is calculated by changing parametrically the slow varying quantities [44, 45, 46, 47, 48].

The QSS distribution depends non-linearly on the electron density, due to three body recombination, and on electron temperature, through rate coefficients of excitation and ionization by electron impact. On the other hand, the dependence on the population of the ground state is linear. As a consequence the ratio

\[ b_i = \frac{n_i}{n_i^{\text{Saha}}} = r_0^i(n_e, T_e) + r_1^i(n_1) \quad (3) \]

where \( r_0^i \), which accounts for the contribution of electron–ion recombination, is calculated neglecting the excitation from the ground state \( (n_1=0) \), while \( r_1^i \), due to the excitation from the ground states, do not consider the recombination processes \( (n_{H^+}=0) \). The QSS distribution is obtained by the cooperative effects of these processes with transitions from excited states due to electronic collisions and radiative decay [46, 49]. A given level i-th reaches the Saha equilibrium when the \( b_i = 1 \). Applying this condition to 3, it is possible to calculate the threshold electron density \( n_e^h \) such that the levels with principal quantum number \( i > h \) are in Saha–Boltzmann partial equilibrium which has been related to electron temperature by the equation [49, 50]

\[ n_e^h \propto T_e^{\gamma/\beta} \quad (4) \]

Different authors (see for example [46, 49, 50]) reports different values for the coefficients \( \gamma \) and \( \beta \), depending on the cross sections and Einstein coefficients used.

In figure 17 the normalized distributions \( f^{\text{QSS}} = \frac{n_i}{g_in_H} \), being \( g_i = 2i^2 \) the statistical weight and \( n_H \) the total density of the hydrogen atoms) calculated under QSS approximation for \( n_1 = 10^{16} \text{ cm}^{-3} \) and varying \( T_e \) between 1 eV–5 eV and \( n_e \) between \( 10^{12} \text{ cm}^{-3}–10^{15} \text{ cm}^{-3} \). In figure 17a the dependence of the QSS distribution on electron density has been analyzed for \( T_e = 1 \text{ eV} \). For low values of \( n_e \) underpopulated tails are observed, being the plasma in ionization regime. Increasing the electron density, the QSS distribution approaches the equilibrium.

Nevertheless, even if the atomic excitation from the ground state becomes more effective by increasing the electron temperature (see figure 17b for \( n_e = 10^{12} \text{ cm}^{-3} \)), the distribution does not approach the equilibrium, because also the ionization is stronger, and the equilibrium composition is obtained for higher values of the electron density. In fact, increasing the \( T_e \), the population of the first excited state increases as well, but the tail shapes slightly changes relatively to the first excited states, depending mainly on the ionization-recombination disequilibrium. This effect is confirmed by 4, being the transition to equilibrium independent of the density of the ground state.
The limits of the QSS approach can arise in systems where the external conditions rapidly changes or in presence of strong space gradients. The first approaches to this problem \cite{51, 52} consider the explicit time evolution of the level population under the assumption of Maxwell electron distributions, based on the assumption of rapidly relaxing EEDF’s. Recently also the effect of non-Maxwellian distributions has been investigated \cite{8}, coupling self-consistently the level kinetics as in \cite{51, 52} with the time dependent Boltzmann equation for free electrons. The model describes at the same time also the time evolution of the electron and atom density.

As test case we have considered an hydrogen plasma with the following initial conditions: \( n_H = 10^{16} \text{ cm}^{-3}, n_e = 10^{12} \text{ cm}^{-3}, T_e=5 \text{ eV}, T_g=1 \text{ eV}, T_H=0.1 \text{ eV} \). In these conditions the electron gas tend to cool down towards the gas temperature by elastic collisions. Due to inelastic collisions, the atoms are excited, heating the level distribution. The level(a) and electron (b) distributions are reported in figure 18. It can be observed that the quasi–stationary level distribution is reached after \( t=10 \text{ ns} \). In the meanwhile, the electron energy distribution is not constant, but due to inelastic collisions, the distribution tail for energies above the first excited state is underpopulated with respect to the Maxwell, reducing the electron temperature to 3.1 eV at \( t=10 \text{ ns} \). In this calculation, the gas composition is practically unchanged, for this reason we can compare the results with the QSS calculations considering the Maxwell distribution at \( T_e=5 \text{ eV} \) (the initial value) and \( T_e=3.1 \text{ eV} \).

Due to non–maxwellian EEDF, the QSS level distributions are more than one order of magnitude higher than the time dependent solution, showing the limit of the maxwellian approximation usually considered in QSS calculation. Moreover, when the level distribution is practically constant, especially for the tail, the high energy EEDF rapidly decreases. It should be also noted that at \( t=10^{-7} \text{s} \) EEDF presents a plateau in the energy range [12-20 eV] due to second-kind collisions between cold electrons and excited atomic levels (see for example \cite{8}).

These results have been used to model the spectra of atomic hydrogen to see the effects of non-equilibrium on the emission line intensity and shape. To calculate the spectra the following processes \cite{4} have been taken into account

- **Absorption and emission in atomic lines (Bound-Bound)**
  \[
  H(n') + h\nu_{nn'} \rightleftharpoons H(n), \quad n' < n
  \]  
  (5)

- **Photoionization and radiative recombination (Bound-Free)**
  \[
  H(n') + h\nu \rightleftharpoons H^+ + e^- (\epsilon')
  \]  
  (6)

- **Bremsstrahlung and inverse Bremsstrahlung due to ions**
  \[
  e^- (\epsilon_i) + H^+ + h\nu \rightleftharpoons e^- (\epsilon_f) + H^+
  \]  
  (7)

Line broadening of atomic hydrogen lines is caused by Stark Broadening from electrons and ions \cite{50, 53, 54}. Free electrons can be quite generally treated in the impact approximations while for \( H^+ \) ions the quasistatic approximation is adequate. At low ion and electron densities other phenomena such as doppler broadening and resonance broadening may give the most important contribution to the line half width. When many different broadening effects are active, the line shape results from convolution of the elementary profiles, and the Voigt function is generally a good approximation. This level of description is accurate enough for plasma kinetic purposes, but it is probably not adequate for detailed spectroscopic analysis. In figure 19 the calculated lines profiles in the Balmer serie are compared with experimental data of Wiese,
Kelleher and Paquette [55] from an experiment at atmospheric pressure. The adopted Stark broadening model overestimates the width of H\(_\beta\), and the Voigt function cannot reproduce the small dip at the center of H\(_\beta\), due to the lack of an unshifted Stark component at line center. Better agreement would require a more detailed consideration of the Stark substructure near the line center [53, 56, 54, 57, 58, 59], but in this case available theories does not lead to analytical expressions for the line profile.

Simulated Balmer lines are reported in figure 20, corresponding to the level distributions of figure 18 at t=10\(^{-8}\) s and the QSS results at \(T_e=3.1\) eV. Moreover, comparison is also made with the spectrum obtained using a Boltzmann distribution at \(T_H=3.1\) eV. The latter is several order of magnitude larger than the two non-equilibrium calculations because it does not take into account the underpopulation of higher excited states, due to the ionizing regime. On the other hand the difference between the time-dependent and QSS calculations reflect the already discussed effect of non-equilibrium EEDF on level populations, and thus on the emissivity. Finally, due to the low electron density, Stark broadening is not very effective, resulting in very sharp line shapes.

![Figure 17](image_url)

**Figure 17.** Level distribution function of hydrogen atoms as a function of level energy under QSS approximation. (a) at \(T_e=1\) eV, for different electron densities; (b) at \(n_e=10^{12}\) cm\(^{-3}\), for different electron temperatures.
Figure 18. Time evolution of (a) excited hydrogen level distribution as a function of principal quantum number and of (b) EEDF as a function of electron energy (initial conditions: \( T_e = 5 \) eV, \( T_g = 1 \) eV, \( n_e = 10^{12} \) cm\(^{-3}\), \( n_1 = 10^{16} \) cm\(^{-3}\)). In (a) a comparison with results obtained under QSS approximation for \( T_e = 5 \) eV and \( T_e = 3.1 \) eV is also reported.

Figure 19. Comparison of the results from the spectral model described in [4] and the experimental data of Wiese et al. [55].
Figure 20. Plasma emissivity in the Balmer lines using different models to calculate the plasma composition and excited states distribution. The lines are indexed with the principal quantum number of the upper state, (a) lines from $n=3$ to $n=6$ (b) lines from $n=7$ to $n=11$. 
6. Conclusions

In this paper we have presented different case studies emphasizing the linking between spectroscopical measurements, atomic and molecular physics and kinetic models. Several non-equilibrium cold plasma conditions, have been discussed, including RF inductive plasma discharges, hollow cathode corona discharges, multipole magnetic discharges, RF parallel plate reactors. Different spectroscopic techniques (CARS, VUV and emission spectroscopy) have been used to measure vibrational and rotational temperatures as well as the distribution of the whole vibrational ladder. All the results emphasize the relevance of the vibrational degree of freedom, in determining the properties of the cold plasma. A particular attention is dedicated to the characterization of the VDF and its coupling a suitable Boltzmann equation to describe EEDF, either under local approximation or including non-local effects.

Simultaneously, efforts are devoted to describe the dependence of dissociative–excitation cross sections on the vibrational quantum number of the initial state (either the ground or excited triplets). Different observations give an indication of the primary role of atomic hydrogen in relaxing the vibrational distribution of H₂ molecules so that the knowledge of the velocity distribution of atoms, ground and excited, and protons becomes essential. On the other hand, these distributions are shown, in all the reported cases, to be strongly affected by the vibrational content of molecules, which in general spreads the translational distribution function towards higher energies.

Finally a collisional radiative model for excited atomic levels is presented and discussed with particular attention on the coupling of excited state kinetics and Boltzmann equation for EEDF. This study is in particular devoted to shed light on the non equilibrium distributions for quasi-stationary and time-dependent plasma conditions.

The presented results, even if obtained for cold plasma conditions, can be extended to fusion devices as tokamak, with direct application to divertor and edge plasma. Experimental techniques (CARS, VUV, emission spectroscopy) and theoretical methods (dynamics of elementary processes, Boltzmann and PIC models, chemical and state-to-state kinetics) can be easily shared by the two communities. In conclusion we hope that the present paper can constitute a bridge for deeply connecting cold and fusion plasma communities which only in these last years start interacting.

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