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**Application of collisional-radiative,
atomic-molecular model to
the recombining divertor plasma**

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Application of collisional-radiative, atomic-molecular model to the recombining divertor plasma

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Abstract

Recombination of hydrogen plasma in the divertor volume can be considered as a simple explanation of divertor plasma detachment phenomena experimentally observed on many tokamaks. As will be shown in this report, the presence of rotationally and vibrationally excited molecules significantly enhance the conventional three-body recombination of plasma and expand the plasma temperature and density range responsible for plasma recombination to much higher temperatures and/or lower densities. The effective rate coefficient for plasma recombination due to chemical reactions with molecules, calculated on the basis of generalized collisional-radiative model (CRAMD code), was found to be about 10^{-10} cm³/s in the wide range of plasma temperatures $T_e = 1 - 3$ eV and densities

1. Introduction

Recombination of hydrogen plasma in the divertor volume can be considered as a simple explanation of divertor plasma detachment phenomena experimentally observed on many tokamaks. As will be shown in this report, the presence of rotationally and vibrationally excited molecules significantly enhance the conventional three-body recombination of plasma and expand the plasma temperature and density range responsible for plasma recombination to much higher temperatures and/or lower densities.

Elementary atomic and molecular processes relevant for a divertor plasma will be reviewed. The following reaction chains are found to be predominant in the multi-species plasma recombination:

- (A) multi-step recombination of ion and electron;
- (B) dissociative attachment of electron to molecule with a consequent reaction of mutual neutralization of negative ion and a proton;
- (C) atomic-to-molecular ion conversion with a consequent dissociative recombination of molecular ion.

The chains *B* and *C* are incomplete as only the excited atoms are produced and collisional-radiative (CR) analysis of $H^*(n > 1)$ relaxation to the ground state atom (with the principle quantum number $n = 1$) must be employed.

The set of coupled collisional-radiative models (**CRAMD** code) was used to study the kinetics of destruction and production of following particles: H_2, H_2^+, H, H^- ; taking into account the excitation and CR transitions within the electronic quantum structure of particles. As the molecular reaction rates depend strongly on the vibrational quantum number, V , of the ground state $X^1\Sigma_g^+$ of H_2 and H_2^+ , appropriate CR models include the calculation of the cascades of vibrational excitation via $e - V$, $p - V$, $V - T$, and $E - V$ processes.

We will present the effective rate coefficients for plasma recombination due to the processes involving H^- and H_2^+ ions, calculated as a function of plasma density and temperature. A comparison of these coefficients with the three-body ion-electron recombination rate coefficient will be given. The influence of enhanced plasma recombination upon the plasma state in the divertor will be discussed.

2. Atomic and molecular processes relevant for divertor plasma

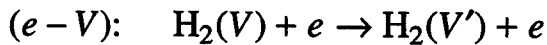
The plasma in the tokamak divertor is a very interesting variety of laboratory plasmas. The typical *ionizing* plasma observed in the high temperature ($T_e \geq 100$ eV) scrape-off-layer has a tend to become the *recombining* plasma in the vicinity of neutralizing plates. The possibility of such a dramatic change in the plasma conditions has been recently demonstrated in the experiments carried out on ALCATOR C-mod and DIII-D tokamaks with a detached plasma. The low-temperature ($T_e < 5$ eV) recombining plasma will be the major object for our analysis and modeling.

In this section the list of basic elementary atomic-molecular processes relevant for the reactive edge plasma will be given¹. Most of these processes are recently included into the collisional-radiative models.

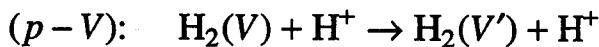
2.1. Collision processes of H₂

Vibrational excitation of hydrogen molecule is due to:

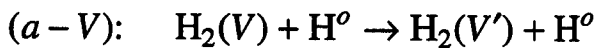
- electron impact



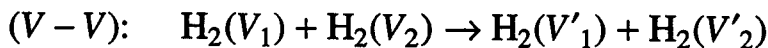
- proton impact



- collision with an atom

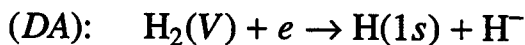


- collision with a molecule



The molecule can be destructed as a result of:

- Dissociative attachment

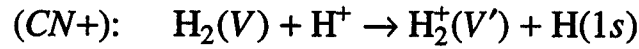


¹in writing the reaction, the following symbolic notations were used: H stands for hydrogen element; * denotes the excited state; V with any index stands for the vibrational quantum number; X is for the ground electronic state of molecule; E is the electronically excited state on molecule or molecular ion; n denotes the principle quantum number for an atom.

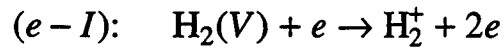
- Pure dissociation



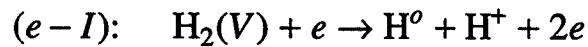
- Increasing conversion



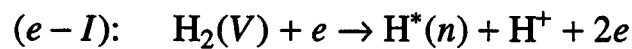
- Ionization



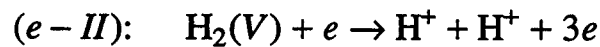
- Dissociative ionization



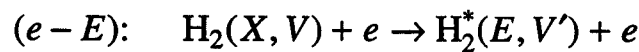
- Dissociative ionization with excitation



- Double ionization



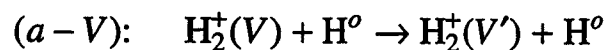
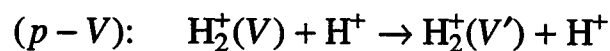
Electronically excited molecules can appear due to inelastic collisions with electrons:



Electronically excited molecules are unstable in plasma, their decay (with characteristic time $< 10^{-9}$ s) is mainly due to the processes of predissociation and spontaneous radiative transitions with respect to the low-lying electronic states.

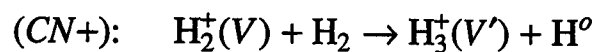
2.2. Collision processes of H_2^+

Vibrational excitation processes are:

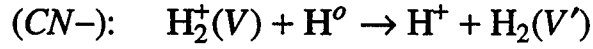


The basic chemical reactions for molecular ion are as follows:

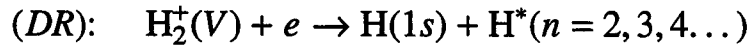
- Increasing conversion



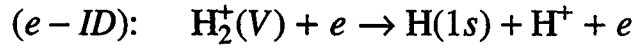
- Decreasing conversion



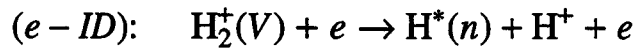
- Dissociative recombination



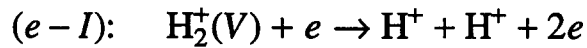
- Pure dissociation



- Dissociative excitation



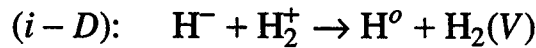
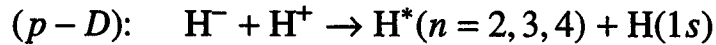
- Dissociative ionization



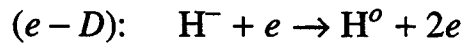
2.3. Collision processes of H^-

The following processes are responsible for the negative ion destruction:

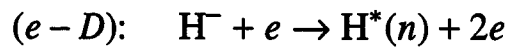
- Mutual neutralization of ions



- Electron-impact detachment



- Electron-impact detachment with excitation

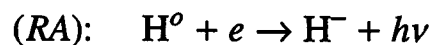


- Atomic-impact detachment

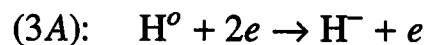


Along with generation of negative ions via dissociative attachment to molecules, H^- can be produced due to:

- Radiative attachment



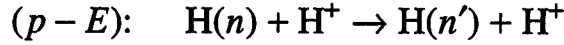
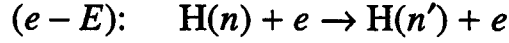
- Three-body associative attachment



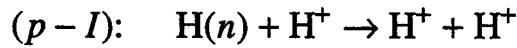
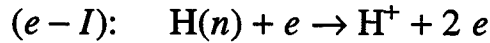
2.4. Collision processes of hydrogen atom

The "standard" set of reactions involving hydrogen atom contains:

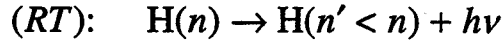
- Excitation



- Ionization

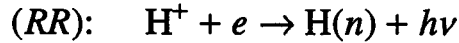


- Spontaneous radiative transitions

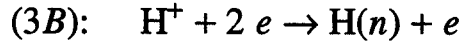


Two fundamental processes contribute to plasma recombination:

- Radiative recombination



- tree-body electron-impact recombination



3. Collisional-radiative model for hydrogen molecule

In this section we will derive the set of basic equations describing the collisional-radiative kinetics of excitation/de-excitation of vibrational levels for the hydrogen molecule in its ground-state.

3.1. General equations for H_2 ground-state

Let's denote by $[\text{H}_2(X, V)]$ the concentration of hydrogen molecules in the vibrational level V of ground electronic state $X \equiv X^1\Sigma_g^+$. This X -state has fifteen vibrational levels with $V = 0 - 14$. The typical equation describing the time evolution of $[\text{H}_2(X, V)]$ density can be written in the following form:

$$\frac{d [\text{H}_2(X, V)]}{dt} + DT(X, V) = \quad (1)$$

$$\begin{aligned}
& - [\text{H}_2(X, V)] \cdot \left(S_{e-D}^V \cdot N_e + S_{DA}^V \cdot N_e + S_{CN}^V \cdot [\text{H}^+] + S_{e-I}^V \cdot N_e \right) + G_{coll}(X, V) \\
& - [\text{H}_2(X, V)] \cdot \sum_{V' \neq V} \left[S_{e-V}^{V \rightarrow V'} \cdot N_e + S_{p-V}^{V \rightarrow V'} \cdot [\text{H}^+] + S_{a-V}^{V \rightarrow V'} \cdot [\text{H}^o] \right] \\
& + \sum_{V' \neq V} [\text{H}_2(X, V')] \cdot \left[S_{e-V'}^{V' \rightarrow V} \cdot N_e + S_{p-V'}^{V' \rightarrow V} \cdot [\text{H}^+] + S_{a-V'}^{V' \rightarrow V} \cdot [\text{H}^o] \right] \\
& - \left\{ [\text{H}_2(X, V)] \cdot N_e \cdot \sum_{E \neq X} \sum_{V_E} S_{e-E}^{V \rightarrow V_E} - \sum_{E' \neq X} \sum_{V_E} [\text{H}_2(E', V_E)] G_{E' \rightarrow X}^{V_E \rightarrow V} \right\}
\end{aligned}$$

Here N_e , $[\text{H}^+]$, $[\text{H}^o]$ are the densities of electrons, protons and hydrogen atoms, respectively; S_{α}^V is the rate coefficient for the reaction of type $\alpha = e - D, DA, CN, e - I$, due to which hydrogen molecule converts into another sort of particles; $S_{\alpha}^{V \rightarrow V'}$ is the rate coefficient for the reaction of type $\alpha = e - V, p - V, a - V$, which lead to the change in the vibrational quantum number of H_2 ground state (i.e. the collisional transitions from V to V' , $V \neq V'$). The term $G_{coll}(X, V)$ implicitly includes all possible reactions in which the $X \ ^1\Sigma_g^+(V)$ state molecule is produced (such as the processes detailed balanced with respect to the reactions $DA, CN, e - I, e - D$, the reactions of association in collision of three heavy particles and e.t.c.). Two terms in the curved brackets describe, respectively, the sink due to excitation of vibrational levels of upper electronic states E of hydrogen molecule and the source due to spontaneous radiative decay transitions from the excited E' -states back into the ground X -state. Index E runs through all bounded electronic states. According to selection rules the index E' includes only singlet states². In these terms $[\text{H}_2(E', V_E)]$ denotes the density of electronic state E and V_E is the vibrational quantum number corresponded to the state E , the quantity $G_{E' \rightarrow X}^{V_E \rightarrow V}$ defines the probability for the transition. The second term $DT(X, V)$ in the *lhs* denotes any other terms which may appear in the transport equation, say, due to convection or collisions of another type (for

² among the singlet series the dominant contribution to radiative transitions give the low-lying resonant states $E' = B, C, B', B'', D, D'$. Characteristic times for these $E' \rightarrow X$ transitions are very short $< 10^{-9}$ s and may effectively compete with the collision times. Radiative transitions between triplet states are also important, but in this case the final state is usually $b^3\Sigma_u$ repulsive state and the transition immediately results in the subsequent dissociation.

example, elastic scattering) than those included into the *rhs*.

The electron-impact dissociation term has the form

$$S_{e-D}^V = \sum_{E'} S_{e-D}^V(E'),$$

where index E' runs over all possible electronic transitions from vibrational level V of X either to the repulsive states (for example, the $b^3\Sigma_u^+$ term, and some Rydberg's auto-ionizing states) or to the repulsive part of potential curves of bounded electronic states (i.e., excitation above the dissociation limit). The detailed form of the term which describe the atomic-to-molecular conversion reaction are as follows:

$$S_{CN}^V(X \rightarrow X_I) = \sum_{\alpha} \sum_{E'} S_{CN_{\alpha}}^{V \rightarrow V_I},$$

where the double summation stands for all channels CN_{α} of the atomic-to-molecular conversion reaction and for all final vibrational states V_I of ground-state $X_I \equiv X^2\Sigma_g^+$ of molecular ion H_2^+ . In general case, the effective term

$$S_{e-I}^V = S_{e-DI}^V + \sum_{E_I} S_{e-E_I}^V + \sum_{V_I} S_{e-I}^{V \rightarrow V_I},$$

which is responsible for the electron impact ionization, includes: i) bound-bound electronic transition between X and X_I states (rate $S_{e-I}^{V \rightarrow V_I}$); ii) bound-free electronic transitions into the vibrational continuum of molecular-ion ground state; ($S_{e-E_I}^V$); iii) dissociative ionization with excitation of all repulsive states of H_2^+ (rate S_{e-DI}^V).

3.2. Application to divertor plasma conditions

Under recombining plasma conditions typical for the low-temperature plasma in the tokamak divertor, the set of CR equations (1) can be significantly simplified. The appropriate simplifications will be discussed here.

First of all it is important to note, that in *Eq.* (1) we skip the possible terms associated with spontaneous radiative transitions between rotationally-vibrationally excited levels of X-state of H_2 , because their probability ($< 10^{-7}$ s) is very small compared to the frequency of any collisional process considered above. We also neglect with the so-called $V - V$ terms which describe the vibrational quanta exchange in the collision of two molecules. This terms will necessarily appear in *Eq.* (1) if it is employed to treat the

conditions of plasma-chemical reactors [1] and molecular lasers [2]. In our case, the characteristic frequency of $V - V$ relaxation is about the same order of magnitude as that for the $V - T$ ($a - V$ in our definition) process³, and at the same time it is much smaller than the frequency of $e - V$ relaxation.

If the electron temperature is high enough $T_e \leq 10$ eV, then the excitation of upper electronic states of H_2 gives a very "fast" mechanism (via the consequent radiative transitions $E \rightarrow X$) for production of X -state molecules in the high vibrational levels⁴. As it has been discussed in [3,4], The chain of reactions $X(V) \rightarrow E \rightarrow X(V')$ may play important role in H_2 vibrational kinetics in the plasma of negative ion sources. But this is not our case. In the divertor plasma the $X \rightarrow E \rightarrow X$ transitions will increase many times the effective rates for molecule dissociation and ionization, whereas the CR rates responsible for plasma recombination will strongly decrease in the high temperature range. In the divertor region in which the molecular processes are expected to affect the plasma recombination the electron temperature is $T_e < 5$ eV. In this low temperature range the excitation rate of upper electronic states of H_2 molecule is found to be small compared to the rate of excitation of the lowest $b^3\Sigma_u^+$ fully-repulsive state [5]. Hence, in the present calculations we neglect in Eq. (1) with the terms within the curved brackets in the *rhs* and remain in the S_{e-D} term only the contribution of dissociation via $b^3\Sigma_u^+$ state excitation. By the same reasons we exclude from our consideration the electron-impact molecule ionization term S_{e-I} .

³ the gas temperature in the divertor plasma is expected to be very high $T_{m,a} = T_i = T_e/2$ due to elastic scattering collisions, so the cross-sections for both $V - V$ and $V - T$ will pass their maximal value in energy dependence and starts to slow down. As the maximal values for both cross-sections are known with a relatively low accuracy and have the same characteristic scale of about few atomic units πa_{Bohr}^2 and as it has already been mentioned the densities of atoms and molecules in divertor plasma are also comparable, the relaxation frequencies of $V - V$ and $V - T$ processes will be approximately equal in the temperature range under consideration. In this aspect, we believe that the inclusion $V - V$ in addition to $V - V$ process will not increase the accuracy of our calculations and will not affect significantly on the vibration-level population. It is also important to note that by neglecting with $V - V$ terms our problem becomes linear with respect to hydrogen molecules density.

⁴ additional feature of $X(V) \rightarrow E \rightarrow X(V')$ reaction chain is that the effective rate coefficient may depend on the difference $|V - V'|$ much more weakly than in the case of $e - V$ vibrational excitation via H_2 resonance. The fist process [3] has a tend to share the vibrational excitation between a broad number of adjacent levels, whereas the rate coefficient of $V \rightarrow V'$ transition due to $e - V$ collisions approximately exponentially decrease with the increase in $|V - V'|$.

Numerous processes of association in many-heavy-particles collision (let's mention, for example, $H^+ + 2H^o = H_2^+ + H^o$, $H^+ + 2H^o = H_2 + H^+$, $H^+ + H^- + H^o = H_2 + H^o$, *e.t.c*) may also take place. These reactions are very interesting for low-temperature plasma chemistry and are usually significant at a very low temperatures $T_h \ll 1$ eV and at high gas densities. But even under favorable conditions the rate constant ranges from 10^{-31} to 10^{-28} cm⁶/s. It is clear that under divertor conditions the effect of reactions of such a type will be negligible small with respect to the resonant processes. In comparison to the direct processes, such as *DA, CN*, the contribution of their detailed-balanced processes are calculated to be small enough as the highly reactive products H^- , H^* , H_2^+ , strongly interact with a plasma and the relative concentration of these particles gets small compared to the H^+ and H_2 . Discussed argument allow us to neglect also in *Eq. (1)* with the term G_{coll} .

In summary we could mention that among the numerous collisional terms in the *rhs* of *Eq. (1)* only few of them are important in describing the recombining divertor plasma. All terms, which we found to be necessarily remained, correspond to the resonant, highly efficient processes of molecule interaction with a plasma.

3.3. Quasi-stationary approximation

In general, in order to determine the densities of vibrational excited molecules [$H_2(X, V)$] one must solve the system of coupled differential equations (1) written for each vibrational level of *X*-state of H_2 . The detailed solution of this problem is not the aim of given report. Here we are interesting only in the detailed investigation of the simplest, quasi-stationary (QS) solution for the problem of collisional populating of vibrational levels of hydrogen molecule. On the basis of QS approach one can calculate the effective rate coefficients for the leading molecular process taking into account the effect of vibrational excitation of molecules.

Originally, the quasi-stationary approach has been applied to the collisional-radiative model for hydrogen atom reactions by Bates *et. al* [6]. In the case of hydrogen atoms, the relaxation time for small density perturbations of the excited electronic states from their quasi-steady values is by orders of magnitude shorter than the characteristic times for a change in the ground-state density and in the density of continuum. Hence, it is expected (and detailed modeling confirm the validity of this approach) that quasi-

stationary populating of excited states takes place under realistic plasma conditions. The validity of application of quasi-stationary approximation in traditional manner to the system of vibrational rate equations is less certain⁵.

Applying the standard, quasi-stationary approximation to our system of rate equations formally, we neglect with all terms in the *lhs* of *Eq. (1)* for the vibrational excited levels ($V > 0$), whereas for the base vibrational level $V = 0$ of ground-state hydrogen molecule all terms we could save. Then, the relative population

$$\rho_X^V = [\text{H}_2(X, V)] / [\text{H}_2(X, V = 0)] \quad (2)$$

of each excited vibrational level $V > 0$ with respect to the lowest level can be easily obtained from the system of fourteen algebraic equations:

$$\begin{aligned} & \rho_X^V \cdot \left(S_{e-D}^V \cdot N_e + S_{DA}^V \cdot N_e + S_{CN}^V \cdot [\text{H}^+] \right) \\ & + \rho_X^V \cdot \sum_{V' \neq V} \left[S_{e-V}^{V \rightarrow V'} \cdot N_e + S_{p-V}^{V \rightarrow V'} \cdot [\text{H}^+] + S_{a-V}^{V \rightarrow V'} \cdot [\text{H}^o] \right] \\ & - \sum_{V' \neq V} \rho_X^{V'} \cdot \left[S_{e-V'}^{V' \rightarrow V} \cdot N_e + S_{p-V'}^{V' \rightarrow V} \cdot [\text{H}^+] + S_{a-V'}^{V' \rightarrow V} \cdot [\text{H}^o] \right] = \\ & = \left[S_{e-V}^{0 \rightarrow V} \cdot N_e + S_{p-V}^{0 \rightarrow V} \cdot [\text{H}^+] + S_{a-V}^{0 \rightarrow V} \cdot [\text{H}^o] \right], \end{aligned} \quad (3)$$

$$V = 1, \dots, 14.$$

Here in comparison with *Eq. (1)* we neglect with some insufficient collisional terms as has been discussed before.

Let's define formally the total density of hydrogen molecules in the ground state as

$$[\text{H}_2(X)] \equiv \left(1 + \sum_{V>0}^{V_{\max}} \rho_X^V \right) \cdot [\text{H}_2(X, V = 0)] \quad (4)$$

then the summation of all equations of the system (4) for $V > 0$ together with equation (1) for the base vibrational level $V = 0$ results in the following

⁵ a more realistic model based on self-consistent calculation of quasi-stationary "vibrational" temperature is under development now.

equation:

$$\frac{d [\text{H}_2(X)]}{dt} + \overline{DT}(X) = - [\text{H}_2(X)] \cdot \left(\tilde{S}_{e-D} \cdot N_e + \tilde{S}_{DA} \cdot N_e + \tilde{S}_{CN} \cdot [\text{H}^+] \right) \quad (5)$$

where effective rate coefficients (also called CR rates) for the destructive molecular processes are defined and calculated as follows:

$$\tilde{S}_{e-D} = \left(S_{e-D}^{V=0} + \sum_{V>0}^{V_{\max}} \rho_X^V S_{e-D}^V \right) \cdot \left(1 + \sum_{V>0}^{V_{\max}} \rho_X^V \right)^{-1} \quad (6a)$$

$$\tilde{S}_{DA} = \left(S_{DA}^{V=0} + \sum_{V>0}^{V_{\max}} \rho_X^V S_{DA}^V \right) \cdot \left(1 + \sum_{V>0}^{V_{\max}} \rho_X^V \right)^{-1} \quad (6b)$$

$$\tilde{S}_{CN} = \left(S_{CN}^{V=0} + \sum_{V>0}^{V_{\max}} \rho_X^V S_{CN}^V \right) \cdot \left(1 + \sum_{V>0}^{V_{\max}} \rho_X^V \right)^{-1} \quad (6c)$$

If all ρ_X^V coefficients are calculated, one can obtain the function $G_{\text{H}_2 \rightarrow \text{H}_2^+}(V_I)$ describing the distributed source of vibrational excited molecular ions produced due to conversion reactions:

$$G_{\text{H}_2 \rightarrow \text{H}_2^+}(V_I) = \left(S_{CN}^{V \rightarrow V_I} + \sum_{V>0}^{V_{\max}} \rho_X^V S_{CN}^{V \rightarrow V_I} \right) \cdot \left(1 + \sum_{V>0}^{V_{\max}} \rho_X^V \right)^{-1} \quad (7a)$$

and the source function $G_{\text{H}_2 \rightarrow \text{H}^-}$ for the negative ions generation:

$$G_{\text{H}_2 \rightarrow \text{H}^-} = \left(S_{DA}^{V=0} + \sum_{V>0}^{V_{\max}} \rho_X^V S_{DA}^V \right) \cdot \left(1 + \sum_{V>0}^{V_{\max}} \rho_X^V \right)^{-1} \quad (7b)$$

4. Collisional-radiative model for H_2^+ molecular ion

The set of state-to-state transition rate equations for the ground electronic state $X_I \equiv X^2\Sigma_g^+$ of hydrogen molecular ion can be presented in the following view:

$$\frac{d [\text{H}_2^+(X_I, V_I)]}{dt} + DT_I(X_I, V_I) = \quad (8)$$

$$\begin{aligned}
& - [\text{H}_2^+(X_I, V_I)] \cdot \left(S_{e-ID}^{V_I} \cdot N_e + S_{DR}^{V_I} \cdot N_e + S'_{CN}^{V_I} \cdot [\text{H}^o] \right) + G_{coll}^I(X_I, V_I) \\
& - [\text{H}_2^+(X_I, V_I)] \cdot \sum_{V'_I < V_I} A^{V_I \rightarrow V'_I} + \sum_{V'_I > V_I} [\text{H}_2^+(X_I, V'_I)] \cdot A^{V'_I \rightarrow V_I} \\
& - [\text{H}_2^+(X_I, V_I)] \cdot \sum_{V'_I \neq V_I} \left[S_{\alpha-V_I}^{V_I \rightarrow V'_I} \cdot N_\alpha \right] + \sum_{V'_I \neq V_I} [\text{H}_2^+(X_I, V'_I)] \cdot \left[S_{\alpha-V_I}^{V'_I \rightarrow V_I} \cdot N_\alpha \right]
\end{aligned}$$

Here $V_I = 0 - 18$ is the vibrational quantum number which identifies the vibrational levels for X_I state; $S_{DR}^{V_I}$ is the rate for dissociative recombination; $S_{e-ID}^{V_I}$ is the rate for molecular ion dissociative excitation under the electron-impact collision; $S'_{CN}^{V_I}$ is the rate for molecular-to-atomic ion conversion; $S_{\alpha-V_I}^{V_I \rightarrow V'_I}$ is the rate coefficient for the transition $V_I \rightarrow V'_I$, $V_I \neq V'_I$ within the vibrational structure of X_I state due to the collision of particle $\alpha = e, p, a$, with a molecular ion; $A^{V_I \rightarrow V'_I}$ denotes the probability of spontaneous radiative transition between the rotationally-vibrational levels $V_I \rightarrow V'_I$, $V_I > V'_I$ of molecular ion.

The term $G_{coll}^I(X_I, V_I)$ describes the effective source of collisional generation of molecular ions in the vibrational level V_I of the ground-state. Detailed structure of source term is as follows:

$$\begin{aligned}
G_{coll}^I(X_I, V_I) &= [\text{H}_2(X)] [\text{H}^+] \cdot G_{\text{H}_2 \rightarrow \text{H}_2^+}(V_I) \quad (9) \\
&+ [\text{H}_2(X)] N_e \cdot \sum_V S_{e-I}^{V \rightarrow V_I} + [\text{H}_2(E')] N_e \cdot \sum_{E'} S_{e-E'}^{V_E \rightarrow V_I} P_{auto}(E', V_E) \\
&+ [\text{H}^*(n)] [\text{H}^o] N_e \cdot \sum_n R_{HH}^n(V_I)
\end{aligned}$$

where the G_{CN} is defined by Eq.(7a) and characterizes the atomic-to-molecular ion conversion process; the second term describes the electron-impact ionization of H_2 (bound-bound transition); the third term stands for the process of excitation of electronic states E' of H_2 with subsequent auto-ionization into the bound vibrational levels of molecular ion, P_{auto} is the probability of auto-ionization; and the last term deals with the 3-body associative ionization process connected with the dissociative recombination by the detailed balance principle, R_{HH}^n is the 3-body rate of $\text{H}^*(n) + \text{H}^o + e = \text{H}_2^+(V_I) + e$.

As in the case of hydrogen molecule it is possible to make several simplifications in the *Eqs. 8, 9* according to the typical plasma conditions in the divertor region.

Hydrogen molecular ion has no dipole moment and quadrupole transitions are rather weak ($A < 10^{-7}$ s) and in *Eq. 8* one can neglect with appropriate terms. This is important fact as it makes our system of rate equations linear with respect to particles density.

Hydrogen molecular ion has no resonant states responsible for the effective vibrational excitation due to electron attachment, so in the last two terms of *Eq. 8* only the collisions of H_2^+ with hydrogen atoms and protons are possible, i.e $\alpha = p, a$.

In order to be consistent with simplified assumptions made for H_2 reactions, in *Eq. 9* we will get off the terms associated with the electron-impact ionization and excitation of auto-ionizing states. As the density of H^* is expected to be small compared to the electron density N_e , the 3-body associative ionization term R_{HH}^n we will also assume to be negligible small. As a result the generation of molecular ions in the divertor plasma will be predominantly due to atomic-to-molecular ion conversion.

Let's discuss now the application of the quasi-stationary approximation to the CR model (*Eqs. 8, 9*) for a molecular ion. As soon as under typical divertor plasma conditions the source term *Eq. 9* was found to be predominantly coupled to the collisional kinetics of ground-state molecule and at the same time the characteristic collisional rates for any vibrational level of H_2^+ exceed by more than an order of magnitude the characteristic rate of vibrational excitation (transition $V = 0 \rightarrow V = 1$) of ground-state molecule, then we can apply the quasi-stationary treatment to all vibrational states of molecular ion including the base level $V_I = 0$.

Defining the relative population $\rho_I^{V_I}$ of vibrational levels of H_2^+ in terms of ground-state hydrogen molecule density

$$\rho_I^{V_I} = [H_2^+(X_I, V_I)] / [H_2(X)] , \quad (10)$$

the following set of algebraic equations for the calculation of coefficients $\{\rho_I^{V_I}, V_I = 0, \dots, 18\}$ can be derived on the basis of *Eq. 8* under QS conditions:

$$\begin{aligned}
& - \rho_I^{V_I} \cdot \left(S_{e-ID}^{V_I} \cdot N_e + S_{DR}^{V_I} \cdot N_e + S_{CN}^{V_I} \cdot [H^o] \right) \\
& - \rho_I^{V_I} \cdot \sum_{V'_I \neq V_I} \left[S_{\alpha-V_I}^{V_I \rightarrow V'_I} \cdot N_\alpha \right] + \sum_{V'_I \neq V_I} \rho_I^{V'_I} \cdot \left[S_{\alpha-V_I}^{V'_I \rightarrow V_I} \cdot N_\alpha \right] \\
& + [H^+] \cdot G_{H_2 \rightarrow H_2^+}(V_I) = 0.
\end{aligned} \tag{11}$$

Important information is the distribution of excited hydrogen atoms produced as the result of successive dissociative recombination of molecular ions. Knowing the local coefficients $\rho_I^{V_I}$, one can calculate the source term of excited hydrogen atoms distributed over the principle quantum number n :

$$G_{H_2 \rightarrow H_2^+ \rightarrow H^*}(n) = \sum_{V_I} \left[\rho_I^{V_I} \cdot S_{DR}^{V_I}(n) \right] \tag{12}$$

where $S_{DR}^{V_I}(n)$ is a partial rate coefficient for dissociative recombination with production of excited atoms in particular quantum state.

5. Collisional-radiative model for H^- negative ion

Quantum structure of H^- is very simple. Practically, there exists only one long living resonant state coupled to the ground state of hydrogen atom.

The time evolution of negative ion density, $[H^-]$, can be described by the following equation:

$$\begin{aligned}
\frac{d [H^-]}{dt} = & - [H^-] \cdot \left\{ \sum_{\alpha} N_\alpha \sum_n S_{\alpha-D}^-(n) \right\} \\
& + \left[[H_2(X)] \cdot N_e \cdot G_{DA}^- + [H^o] \cdot N_e \cdot G_{RA}^- + [H^o] \cdot N_e \cdot G_{3A}^- \right].
\end{aligned} \tag{13}$$

Here n denotes the principle quantum number of hydrogen atoms produced in the interaction of H^- with plasma particles; $S_{\alpha-D}^-(n)$ is the rate coefficient for the negative ion desintegration in collision with particle $\alpha = e, p, a$ with production of hydrogen atom in electronic state n , (n is the principle quantum number of atom). Negative ions are produced in collisions and the appropriate source terms stand for: dissociative attachment of electron to a molecule, $G_{DA}^- \equiv G_{H_2 \rightarrow H^-}$ (see Eq. (7b)); radiative electron attachment to an atom (G_{RA}^- is the rate coefficient for $H + e \rightarrow H^- + h\nu$); and 3-body associative electron attachment, $G_{EA}^- = R_{EA} \cdot N_e$, (R_{EA} is the 3-body rate constant

for $H + e + e \rightarrow H^- + e$).

As the negative ion is a very reactive particle (in particular under conditions of divertor plasma) and quasi-stationary treatment of Eq. (13) is a good approach. The QS population then is

$$\rho_{H^-}^s = \frac{N_e G_s^-}{\left(\sum_{\alpha} N_{\alpha} \sum_n S_{\alpha-D}^-(n) \right)} \quad (14)$$

where index $s = DA, EA, EA$ denotes the particular source of negative ions, and the values of relative populations $\rho_{H^-}^s$ are defined in terms of density of initial heavy particle in the reaction s .

The reaction of positive and negative ions mutual neutralization ($\alpha = p$ in Eq. (13)) is of our particular interest. The distributed source of excited hydrogen atoms produced due to this reaction is calculated for $s = DA$ as

$$G_{H_2 \rightarrow H^- \rightarrow H^*}(n) = \rho_{H^-}^{s=DA} \cdot S_{p-D}^-(n) \quad (15)$$

6. Generalized collisional-radiative model

In the previous sections we discussed the CR models for individual particles. The following species was considered: H_2, H_2^+, H^- . The CR model for hydrogen atom has been already discussed many times in literature since [], and our own model do not differ from the standard one very much. This set of CR models is believed to be complete enough⁶ in order to describe the behavior of hydrogen-species plasma and gas in the divertor.

In order to be adequate to the multi-species plasma conditions, all CR models must be incorporated into the generalized CR model. If one neglects with the collisions between the excited particles and assumes that quasi-stationary conditions are met, then such a generalization can be easily done by means of the specific source and sink terms typed $G_{\alpha \rightarrow \beta}^{\gamma}$. These terms describe a collision between α and β particles in which α -particle disappears and the new particle γ appears (α, β, γ stand for an arbitrary

⁶we haven't yet derive the CR model for extremely heavy hydrogen species: H_n, H_n^+ , with $n > 2$. At least, if $[H_2] \leq [N_e]$ and $T_h \approx T_e > 1$ eV one could expect that the characteristic frequency of H_3 production due to conversion reaction (of Langevin type) $H_2^+ + H_2 \rightarrow H_3^+ + H$ will be small compared to the frequency of H_2^+ dissociation.

combination of three particles of different species). The generalized model conserves the the number of particles and satisfies locally the condition of plasma charge neutrality:

$$[N_e] + [H^-] = [H^+] + [H_2^+]$$

Collisional-radiative rate coefficient $k_{rec}^{(m)}$ describing the chain of atomic-molecular processes which lead to plasma recombination can be introduced and calculated⁷ as follows

$$k_{rec}^{(m)} = \sum_n \left[G_{H_2 \rightarrow H^- \rightarrow H^*}(n) \cdot P_{H^* \rightarrow H^o}(n) \right] \quad (16)$$

$$+ \sum_n \left[G_{H_2 \rightarrow H_2^+ \rightarrow H^*}(n) \cdot P_{H^* \rightarrow H^o}(n) \right] [H^+] / N_e$$

Here $P_{H^* \rightarrow H^o}(n, pp)$ is the probability for conversion of electronically excited atom into the ground-state atom. This probability can be obtained by using the CR model for hydrogen atom with a unity source term placed into the electronic level n . As we neglect with radiative transitions for H_2 and H_2^+ , the functions G depend only on plasma and neutral temperatures, whereas the the function P is the strongly depends on many parameters pp of multi-species plasma (namely, on the species temperatures and densities).

7. Code development

The computer realization of the generalized CR model is the **CRAMD** code (the letters stand for **C**ollisional **R**adiative **A**tomical **M**olecular **D**ata). With the help of CRAMD code one can calculate the effective CR rates for the various atomic and molecular processes important under conditions of multi-species, edge plasma.

8. Results of calculations

We employ the CRAMD code to calculate the CR rate coefficients for hydrogen plasma ionization and recombination within the wide range of edge plasma parameters. The results of our calculations are given in Figs. 1-2. Here the CR rates for:

⁷triple transition index in function G appears because the particles H^- and H_2^+ under our simplified assumptions become *translational*

- hydrogen atom ionization (k_{ion}),
- proton-electron recombination, (k_{rec}^p),
- plasma recombination due to chemical reactions with vibrationally excited molecules ($k_{rec}^{(mol)}$),
are displayed.

The calculations show that the plasma chemical reactions of vibrational excited molecules with plasma particles give a very efficient mechanism for plasma recombination. As a result, the CR rate for proton-electron recombination can be enhanced by about two orders of magnitude for plasma temperature of about 1 eV.

As can be seen in Figs. 1-2, the coefficient $k_{rec}^{(mol)}$ reaches its broad maximum at plasma temperature $T_e^m \approx 1.3$ eV and the position of maximum slightly depends on the plasma density variation. The maximal rate for plasma recombination is found to be surprisingly large: $k_{rec}^{(mol)}(T_e^m) \approx 2 \cdot 10^{-10}$ cm³/s for plasma density $N_e = 10^{14}$ /cm³. This magnitude is in a good agreement with our earlier estimations [7] based on a simple diffusive model for the vibrational excitation kinetics of hydrogen molecule.

The observed temperature dependence of $k_{rec}^{(mol)}$ has a simple explanation. Under recombining plasma conditions, electron-impact vibrational excitation is the main process which by populating of highly ro-vibrational levels activate the subsequent molecular processes leading to plasma recombination. Vibrational excitation rate coefficient drops with the decrease in plasma temperature, and the CR rate $k_{rec}^{(mol)}$ has the same temperature dependence in the temperature range below T_e^m . For the plasma temperatures higher than T_e^m , the processes of pure dissociation of molecule become the dominant ones and, as a result, $k_{rec}^{(mol)}$ decreases with the temperature increase.

The increase in plasma density results in the $k_{rec}^{(mol)}$ decrease. The density dependence is determined by the function which give the probability for conversion of electronically excited atom into the ground-state atom. The higher the plasma density, the ionization of excited atoms is more probable.

Let's compare the CR ionization rate k_{ion} with the CR rates for recombination. As one can see in Fig. 1, if plasma temperature go down from 5 to 1 eV, the ionization rate rapidly drops and both recombination rates go up. Proton-electron recombination rate k_{rec}^p becomes equal to the ionization rate

at temperature of about 1.3 eV at which the rate of molecular-activated recombination reaches the maximum. The characteristic plasma temperature T_e^* , at which $k_{rec}^{(mol)} \approx k_{ion}$, is about twice higher than that for proton-electron recombination.

Another important feature of plasma recombination due to molecular processes is that at any temperature the largest magnitudes of rate $k_{rec}^{(mol)}$ attained at low densities, whereas the rate for traditional proton-electron recombination strongly decreases if the plasma density goes down.

9. Conclusions

The generalized collisional-radiative model which involve ground as well as vibrationally and electronically excited states of hydrogen molecule H_2 and molecular ion H_2^+ and hydrogen atom, and negative ions H^- , has been developed. This CR model incorporates extensive atomic-molecular data, including the chemical reactions (such as atomic-to-molecular ion conversion) which have been already found important for various laboratory and astrophysical plasmas.

The computer realization of generalized CR model is the CRAMD code. This code was employed to study the recombining plasma conditions experimentally observed in the tokamak divertor. Our calculations clearly show that the presence of rotationally and vibrationally excited molecules significantly enhance the conventional three-body recombination of hydrogen plasma and expand the plasma temperature and density range responsible for plasma recombination to much higher temperatures and/or lower densities. The effective rate coefficient for plasma recombination due to chemical reactions with molecules was found be surprisingly large, about 10^{-10} cm³/s in the wide range of plasma temperatures $T_e = 1 - 3$ eV and densities. We conclude that the processes of hydrogen plasma recombination in the divertor volume certain conditions may be very strong and must be taken into account for the explanation of divertor plasma detachment phenomena.

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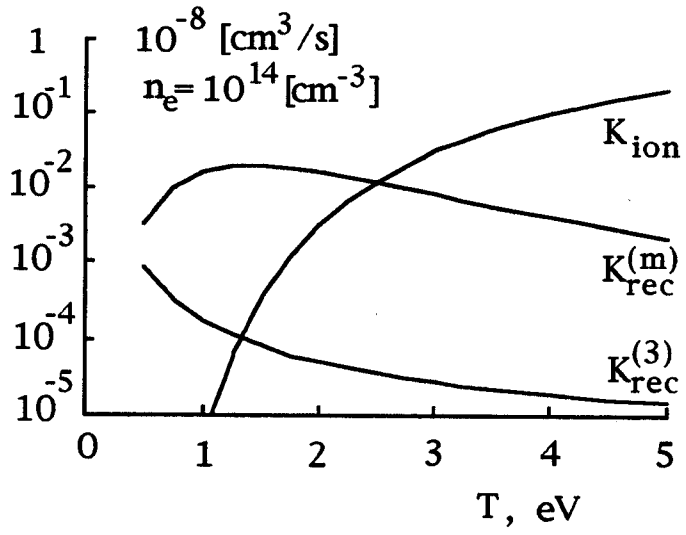


Fig. 1.

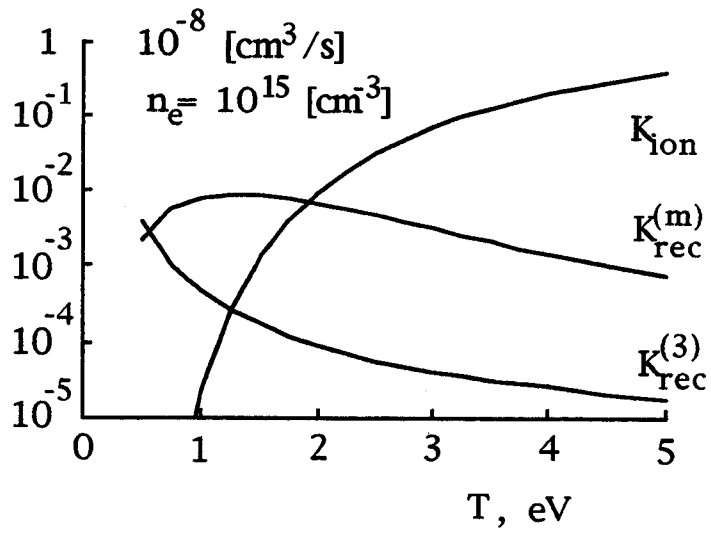


Fig. 2.