

# Vibrational Distribution of H<sub>2</sub>/D<sub>2</sub> Molecules in Low Temperature Plasmas

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## Abstract

Based on the quasi-steady state and quasi-stationary approximation, the vibrational distributions of hydrogen and deuterium molecules in low temperatures are studied. Newest cross section data in the literature are applied while the unavailable data are calculated by applying Gryzinski-method. The modeling shows that the initial absolute slopes of the vibrational distribution curves are increasing functions of the electron temperature when the electron temperature is less than 10 eV. However, this dependence can not be verified by the experiment performed in MAP-II (B. Xiao, PSI-16, [1]). The mechanisms behind this discrepancy are discussed, however, remain unrevealed.

## Keywords:

vibrational distribution, hydrogen molecule, low temperature plasma

## 1. Introduction

Vibrational excitation drastically enhances the negative ion production rate and thus attracts extensive attention in the field of negative ion sources [2,3]. In the edge plasmas in a fusion device, molecular behavior must play an important role. It was in fact, theoretically predicted [4] and experimentally confirmed in a linear plasma device [5] that molecular assisted recombination (MAR) rate can be very effective at plasma temperature as high as 3 eV. This MAR effect causes much less particle flux and thus lower heat flux to the divertor target. The MAR effect is mainly related with the vibrational excitation of molecules.

In this paper, we applied the quasi-steady state and quasi-stationary approximation to model the density distribution of molecules at different vibrational levels to study the vibrational distributions of hydrogen and deuterium molecules. After the description of the model and the included main kinetic processes, we discuss the modeled results and the comparison with the previously reported experiment [1]. This work is still in progress and the further improvement of the model and the applied data is ongoing.

## 2. Model and the kinetic processes

When hydrogen molecules exist in low temperature plasmas, they collide with ions, electrons and neutrals and thus will be excited, dissociated and ionized.

As listed in the Table 1, some of these kinetic processes cause the vibrational excitation or de-excitation of molecules and almost all the processes are influenced by the molecular vibrational level. When the transport time scale is much longer than the characteristic time of the molecules reaching vibrational equilibrium, we can approximate the vibrational population balance by a quasi-steady state and quasi-stationary model,

$$\sum_i \left( \frac{dN_v}{dt} \right)_i = 0. \quad (1)$$

The summation must be performed on all processes which make the generation and depopulation of the molecules in vibrational state  $v$  which varies from 1 to 14 for H<sub>2</sub>. Taking the vibrational ground state as the reference state of which the density is determined by slow process - the transport, the vibrational distribution can be obtained by solving the balance equation (1). Table 1 summarizes all the important processes considered in this paper and their cross section data sources. When the energy of the electrons is low in the order of several electron volts, hydrogen molecule can attach one electron to form the H<sub>2</sub><sup>-</sup> negative ion, mostly in the resonant electronic states of <sup>2</sup>Σ<sub>g</sub><sup>+</sup> and <sup>2</sup>Σ<sub>u</sub><sup>+</sup>. These negative ions can be further dissociated or detach one electron to return to the ground state. The latter process (hereafter referred to e-v) causes the H<sub>2</sub> molecules to gain vibrational quanta, or to say, to be vibrationally excited. The

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Table 1 Kinetic process of H<sub>2</sub>(D<sub>2</sub>) in low temperature plasmas.

e-v	$e + H_2(v) \rightarrow H_2^- \rightarrow e + H_2(w)$	[6]
E-V	$H_2(v) + e \rightarrow H_2(B^1\Sigma_u^+, C^1\Pi_u) + e \rightarrow H_2(w) + e$	[7,23]
p-v	$H_2(v_i) + H^+ \rightarrow H_2(v_f) + H^+$	[8-9]
e-DA	$e + H_2(v) \rightarrow H_2^- \rightarrow H + H^-$	[6]
e-D	$e + H_2(v) \rightarrow H_2(b^3\Sigma_u^+) + e \rightarrow H + H + e$	[7,23]
e-D	$e + H_2(v) \rightarrow H_2(a^3\Sigma_g^+, c^3\Pi_u, e^3\Sigma_g^+, d^3\Pi_u)$	This work
Ionc	$H_2(v) + H^+ \rightarrow H_2^+ + H$	[9-10]
e-DE	$H_2(v) + e \rightarrow H_2(B^1\Sigma_u^+, C^1\Pi_u) + e \rightarrow H + H + e$	[7,23]
e-I	$H_2(v) + e \rightarrow H_2^+ + 2e$	[7,23]
e-ID	$H_2(v) + e \rightarrow H + H^+ + 2e$	[7,23]
v-v	$H_2(v) + H_2(w+1) \rightarrow H_2(v+1) + H_2(w)(v \leq w)$	[11]
v-t*	$H_2(v) + A \rightarrow H_2(w) + A(v > w)$	[11-13]

\* v-t relaxation by H and H<sub>2</sub> is only considered in this paper.

cross sections of e-v process have been calculated by Bardsley and Wadehra [6]. It was shown that this process mainly changes the vibrational level by one. Because the existing data for this process are limited to certain vibrational transitions, they must be extended in order to be applied to the modeling of the vibrational distribution. We adopted a scaling law suggested by Gorse *et al.* [13],

$$\sigma_{1 \rightarrow w} = w\sigma_{0 \rightarrow w-1} (1 < w < 6) \text{ and}$$

$$\sigma_{v \rightarrow w} = \sigma_{v-1 \rightarrow w-1} = \dots = \sigma_{1 \rightarrow w-v+1} (w \geq 2). \quad (2)$$

This scaling approximately reproduces the Bardsley and Wadehra's data [6] of the excitation started from initial states higher than zero at discrete electron energies of 6 and 8 eV.

When the energy of the incident electron is above  $\sim 14$  eV, H<sub>2</sub> can be electronically excited to the higher electronic states. Among these electronic excitations, some lower lying singlet states such as B<sup>1</sup>Σ<sub>u</sub><sup>+</sup> and C<sup>1</sup>Π<sub>u</sub> states can be effective. These electronic states can radiatively return to the ground state. When returning to the ground state, these excitations alone can also make the molecules distribute toward higher vibrational states. In comparison with the e-v process, by these excitations, the vibrational change can be more than one because of the characteristics of the Franck-Condon factors. The contribution of the excitations to the higher electronic states can be neglected because of their small cross sections in low temperature plasmas. The cross sections of E-V processes have been calculated by the impact parameter method and recently were summarized by Celiberto *et al.* [7].

In low temperature plasmas, when the ion temperature is comparable with the electron temperature, the H<sup>+</sup>-H<sub>2</sub>(v) collision can be effective. The cross

sections can be found on the website, <http://www-cfadc.phy.ornl.gov/h2mol/molh2.html>.

When the molecules gain the vibrational quanta from the above mentioned collisions, the quanta can be redistributed via the vibrational-vibrational exchange among the molecules. There is no net gain or loss of the vibrational quanta but the consequent effect is that the molecule distribute toward higher vibrational levels. If the molecules are much denser than the electrons, the exchange would drive the molecules to distribute in the Treanor's function [14,15],

$$N(v) = N_0 \exp\left(-\frac{\bar{\omega}v}{kT_v} + \frac{\bar{\omega}_x v(v+1)}{kT}\right), \quad (3)$$

where  $T_v$  and  $T$  are the vibrational and translational temperatures, respectively.  $v$  is the vibrational level and  $\bar{\omega}$  and  $\bar{\omega}_x$  are the molecular vibrational constants.

The dissociation via the excitation to the triplet repulsive state b<sup>3</sup>Σ<sub>u</sub><sup>+</sup> is the dominant dissociation channel. Ref. [7] has summarized this dissociation cross section data which are based on the Gryzinski semi-classical method. In addition, the excitations to the other triplet states such as a<sup>3</sup>Σ<sub>g</sub><sup>+</sup>, c<sup>3</sup>Π<sub>u</sub>, e<sup>3</sup>Σ<sub>g</sub><sup>+</sup>, d<sup>3</sup>Π<sub>u</sub> are also effective in low temperature plasmas. For these excitations, the complete set of the vibrationally resolved cross sections are not available in the literature. To obtain the complete sets of vibrationally resolved electron impact cross sections we apply Gryzinski semi-classical theory [16,17]. Gryzinski [16] derived an energy gain differential cross section for atomic/molecular excitation, which is expressed as,

$$\sigma(u) = \frac{N_e \times 6.56 \times 10^{-14}}{u^2} \sqrt{\frac{E_i}{(E_o + E_i)^3}} \times \left(1 - \frac{E_o}{E_i} + \frac{4E_o}{3u} \ln [2.7 + \sqrt{(E_i - u)/E_o}]\right)$$

$$\times [1 - (u/E_i)]^{E_o/(E_o+u)} \quad [\text{cm}^2/\text{eV}], \quad (4)$$

where  $E_o$  and  $E_i$  are the kinetic energies of the target and incident electrons, respectively.  $N_e$  is defined as the effective number of mobile electrons, which was discussed in detail in refs. [16,17] and can be adjusted by the experimentally measured cross sections. For a specific transition, the cross section can be obtained by the integration of  $\sigma(u)$  within an energy gain limitation ( $E_1, E_2$ ), as follows:

$$Q = \int_{E_1}^{E_2} \sigma(u) du. \quad (5)$$

The excitation to the triplet states from the ground state is spin exchange excitations which can occur in a way by exchanging the orbital electron with the incident electron. In this scenario, then the energy gain limitations  $E_1$  and  $E_2$  must be,

$$E_2 = E_i + E_{ion} - U_n$$

$$E_1 = \begin{cases} E_i + E_{ion} - U_{n+1} & (E_i \geq U_{n+1}) \\ E_{ion} & (U_n \leq E_i \leq U_{n+1}) \end{cases}. \quad (6)$$

It must also be noted that  $E_i$  in Eq. (6) must be substituted by  $E_i + E_{ion}$  for a spin change excitation. For the molecular excitation, the cross section  $Q$  must be further multiplied by the Franck-Condon factor, which connects the two vibrational levels at the excited and original electronic states as

$$Q_{Av}^{Bv'} = q_{Av}^{Bv'} Q, \quad (7)$$

where  $A$  and  $B$  stand for the lower and upper electronic states, respectively, and  $q$  is the Franck-Condon factor.

In our calculation for the repulsive state  $b^3\Sigma_u^+$ , we applied the potential curve by T.E. Sharp [18]. For the other triplet bonding states, we applied the potential curves in the calculation by Staszwska and Wolniewicz [19]. For the processes related with the D<sub>2</sub> molecules except the excitations to the triplet states, if not available in the literature, we used the same cross sections with H<sub>2</sub>.

### 3. Results and discussion

Figures 1 and 2 show the calculated vibrational distributions of H<sub>2</sub> and D<sub>2</sub> at different electron temperatures. It is seen that there are higher distributions under the medium vibrational levels when the electron temperature is lower both for H<sub>2</sub> and D<sub>2</sub>. However, the experiment with H<sub>2</sub> discharge performed in MAP-II device, which were report earlier [1], showed the opposite trends. In our previous work, the typical experimental conditions are the neutral pressure of 2–12 mTorr and

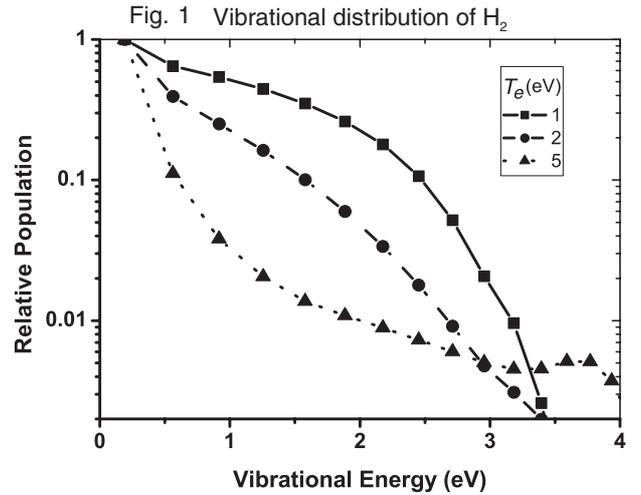
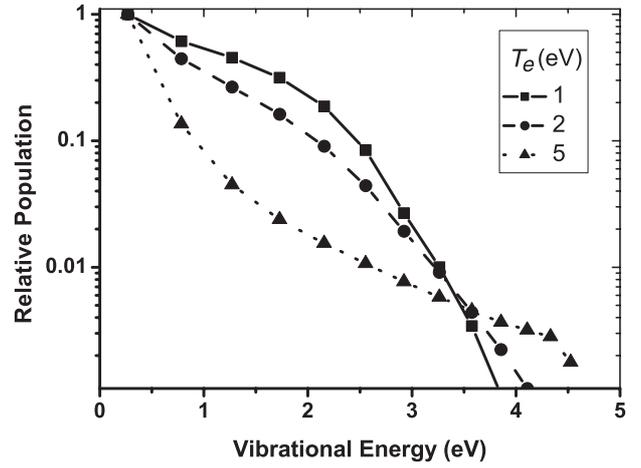


Fig. 2 Vibrational distribution of D<sub>2</sub>

the electron temperature of 2–6 eV. In this experiment, the rotational temperature was also derived from the Fulcher- $\alpha$  band spectroscopy. It was within the range of 300–600 K. The fitting to the observed Fulcher- $\alpha$  band emission showed that the H<sub>2</sub> vibrational temperature is an increasing function of the electron temperature. We have seen in our previous discussion that the vibrational temperature at least reflects the initial slopes of the distribution curve and that any premises used by the experiment analysis should not change this relative dependence of the vibrational temperature on the electron temperatures.

The E-V process is only effective when the magnitude of the electron temperature is higher than  $\sim 10$  eV. Although the p-v process plays important role in low temperature plasmas the exclusion of this process from the modeling does not change the predicted dependency of the vibrational distribution on the electron temperatures [20]. Vibrational-vibrational exchange is only effective in high vibrational levels with the density of molecules much higher than the electron density according to the proposed scaling law by Ref. [11].

It is found that the dominant contribution to the vi-

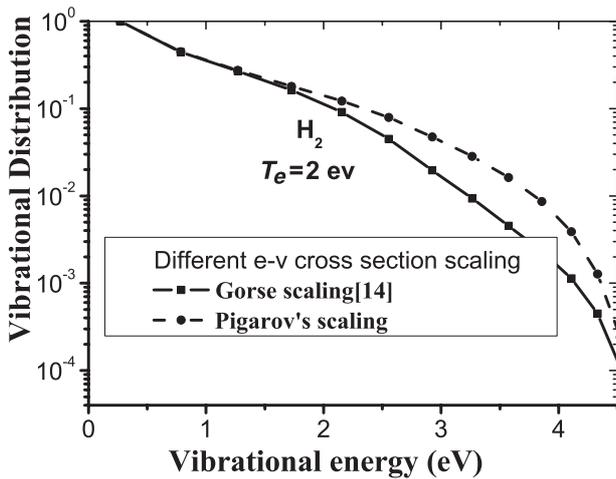


Fig. 3 Comparison of the calculated vibrational distribution based on different e-v cross section scaling.

brational distributions at electron temperatures less than 5 eV is the e-v process. The discrepancy might be caused by the Gorse *et al.* scaling [13] used by us for the e-v cross sections. As a cross checking, we change the scaling to what was suggested by Pigarov [21], the result at electron temperature of 2 eV is shown in Fig. 3. It can be seen that only a slight modification to the distribution is made. At other electron temperatures, the modifications are also small. The modification to the e-v scaling in the modeling did not change our observed dependence. If one checks the Bardsley and Wadehra's [6] cross section data then one find that the nature of e-v process causes the higher vibrational distribution in the lower electron temperatures.

In the experiment in Ref. [1], the vibrational temperatures were measured after the plasmas reached steady-state. There might be influence by the non-thermal high energy electrons, however, it was shown in the experiment in Ref. [22] where the experimental conditions were quite similar to those in Ref. [1], that the high energy tail is low and has negligible effect to the reaction rates considered in this paper.

In the modeling, we only considered the v-t relaxation caused by H<sub>2</sub> and H because they are the main neutral species in the H<sub>2</sub> discharges in MAP-II. The rate coefficients of H + H<sub>2</sub> system are directly from the appendix in Ref. [13]. The experimental determination of H density in MAP-II is difficult and has not been completed yet, so in our modeling, we arbitrarily set the H density to be of the same order as the electron density. As shown in Ref. [13], the v-t rate coefficients of H + H<sub>2</sub> collisions below the gas temperature of 1000 K, are within the orders of  $10^{-11} \text{ cm}^{-3} \text{ s}^{-1}$  which is two orders lower than the e-v rates, i.e.,  $1.9 \times 10^{-9} \text{ cm}^{-3} \text{ s}^{-1}$  for the e-v process from  $v_i = 0$  to  $v_f = 1$  at  $T_e = 3 \text{ eV}$ . So it is reasonable to expect that the arbitrary H density in the

modeling would not cause much error to the modeling result.

The left unknowns are the collisions related with H<sub>3</sub>, H<sub>2</sub><sup>+</sup> and H<sub>3</sub><sup>+</sup> which may contribute to the vibrational excitation of H<sub>2</sub>, however, the information on this issue is very limited. To clarify it will be our future objective.

#### 4. Summary

We have performed the modeling of the vibrational distribution of hydrogen and deuterium molecules in low temperature plasmas. It was shown that the vibrational distribution is higher under the medium vibrational levels when the electron temperature is lower. This does not agree with our previous experiment [1] which showed the opposite dependence. There still exists the gap in our understanding on the mechanisms behind. Our future effort will concentrate on the clarification of the gap between the experiment and the modeling.

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