Heterogeneous and homogeneous hydrogen kinetics in plasma chemistry

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Abstract. A review of gas phase and surface kinetics of hydrogen radicals in plasma chemistry is presented. It is shown that the presence of rovibrationally excited hydrogen molecules strongly influences the mechanisms of the chemical reactions. Both homo- and heterogeneous collisional processes are analysed in that respect. As will be shown, ionizing plasmas are dominated by gas phase rovibrational excitation phenomena. By contrast the kinetics of recombining plasmas are strongly influenced by heterogeneous elementary processes, where they can be distinguished in a natural way. Examples of heterogeneous catalysis in plasmas, i.e. particle excitation phenomena at surfaces, are discussed.

1. Introduction

A special interest in plasma chemistry arises nowadays in the development and characterization of effective sources of reactive hydrogen radicals: vibrationally excited molecules, atoms and ions. Hydrogen radicals are of principal importance in the various schemes for deposition of diamond and diamond-like films [1], for selective etching of the materials [2], and in the deposition and passivation of amorphous and polycrystalline silicon films [3]. Furthermore, the kinetics of hydrogen molecules, atoms and ions in plasmas and on surfaces are of great interest in understanding the processes of H− formation in volume and surface production negative ion sources [4]. In fusion experiments the kinetics of hydrogen species determine the heat losses in the plasmas. The use of highly dissociated hydrogen plasmas has also become a common procedure in the cleaning of inner surfaces of fusion reactors [5]. For a better understanding of hydrogen radicals properties, for optimization of plasma sources and for application in plasma chemistry a detailed study of the plasma kinetics and plasma flow dynamics is necessary. It will be demonstrated that for the hydrogen radical kinetics both gas phase and surface processes are important. The problem consists of separating homo- and heterogeneous reactions, since they occur simultaneously.

In this paper we will concentrate on surface excitation phenomena. In that respect the recombining plasma represents a special interest as it is a candidate for investigating selective radical reactions on surfaces. Since hydrogen ion kinetics have been discussed previously [6], this paper will only cover the kinetics of neutral hydrogen radicals in the plasma: atoms and rovibrationally excited molecules.

2. Hydrogen radicals in ionizing plasma

Most of the experimental and theoretical research on the characterization of a hydrogen plasma has been performed with respect to the ionizing plasma, because of the wide range of applications. In this section we will concentrate on the details of diagnostics and modelling of hydrogen radicals in ionizing plasma systems.

2.1. Hydrogen atoms

2.1.1. Diagnostics. The problem of atomic radical density determination (i.e. the dissociation degree) is one of the most complicated in plasma chemistry. For atomic hydrogen the resonant radiative transitions belong to the vacuum ultraviolet (VUV) part of the spectrum. Therefore sophisticated techniques of VUV coherent and non-coherent absorption spectroscopy have been used for the diagnostics of H atoms properties in the ground state. Strong VUV continuum, radiated by a pulsed gas discharge, has been used in the methods of resonance fluorescence [7] and absorption of continuum radiation [8]. Radiation of the Lyman-α generated by a microwave discharge lamp has been used to measure linear absorption of this line in the positive column of a glow discharge [9]. The method of resonance-enhanced multiphoton ionization (REMPI) [10], the technique of four-wave sum-frequency mixing (FWSM) [11] and the method of coherent anti-Stokes Raman scattering (CARS) [12] were employed to measure the hydrogen atom absolute density emanating from a hydrogen volume source of negative ions. The VUV laser-induced fluorescence (LIF) technique has been applied as a method to measure H atom temperature [13] and density [14–17].
In the case of the excitation of radiative states of atoms and molecules by direct electron impact from the ground electronic state, the method of optical actinometry can be employed for the density determination of radicals ground state [18]. With respect to hydrogen plasma diagnostics optical actinometry has been used to characterize microwave plasma reactors [19,20] and pulse discharges [21], used for diamond synthesis. Others employed 'active' actinometry to determine the dissociation degree of an expanding recombining plasma [22]. Besides spectroscopical techniques, mass spectrometry has also been applied to hydrogen plasma diagnostics (cf for example [23,24]).

Based on the experimental diagnostics and kinetic modelling of ionizing plasma the main mechanism for H atoms production in hydrogen plasmas are believed to include the following:

- direct electron impact dissociation of H$_2$ [18,25];
- collisional step-wise vibrational energy redistribution until the dissociation limit [26];
- dissociative attachment of electrons to vibrationally excited H$_2$ molecules [27-29];
- dissociative recombination of hydrogen molecular ions [30];
- mutual recombination of hydrogen positive and negative ions [31,32];
- dissociative neutralization of hydrogen positive molecular ions on the surfaces [33,34].

Hydrogen atoms are removed from the plasma mainly by the two reactions:

- three-body collisional gas phase recombination [20];
- transport plus wall recombination [10,35-37].

2.2.1. Modelling. Chemical kinetic schemes for pure hydrogen plasmas have been analysed in several papers. However, in most of the models (cf for example [19,20,46,47]) it is assumed that the particle energy distribution functions are Maxwellian, i.e. each component (electrons, ions, neutrals) is characterized by its equilibrium temperature. Strictly speaking, at least for the electrons, this assumption is not valid when the ionization degree is smaller than $\approx 10^{-4}$. An assumption about the equilibrium Maxwellian approximation with respect to hydrogen atoms is rather questionable as well, since a significant density of 'hot' hydrogen atoms can be produced in the reactions of dissociative excitation of H$_2$ and/or dissociative recombination of H$_2^+$. 'Hot' hydrogen atoms have been detected by various techniques in the broad variety of gas discharges (cf for example [40-42]). In view of this such numerical models have limited accuracy. Until now, only a few numerical schemes have been developed where the simulation codes include a simultaneous calculation of the EEDF in the plasma [43-45].

A typical model considers the neutral species (H, H$_2$), positive ion species (H$^+$, H$_2^+$, H$_3^+$) and negative ions H$^-$ which, along with electrons, are allowed to interact through the various reactions. Besides gas phase reactions, surface processes in which particles are excited are shown to be very effective. As has been demonstrated in many papers, recombination on the walls of the reactor should be considered a dominant mechanism for the atomic hydrogen density determination in the plasma. It is generally believed that there is not a direct unambiguous correlation between the reaction kinetics in hydrogen plasmas (including the hydrogen atom production in the bulk) and collisional processes occurring at the walls (see, for example [46,47]).

2.2.1.3. Surface recombination phenomena. Wood and Wise [35] first proved that the actual density of atomic hydrogen in various plasma sources is determined by the recombination probability of atoms on the walls $\gamma (0 \leq \gamma \leq 1)$. The historical importance of the work of Wood and Wise is primarily based on the determination of the recombination coefficients of hydrogen on different metallic surfaces (however, surface properties — such as the crystallographic structure and chemical coverage — were not controlled in these experiments). The measured value for $\gamma$ for different metals increases with the Debye characteristic temperature of the metal. In accordance with that, a free atom is more likely to recombine with one adsorbed on a surface. This means that a hydrogenated surface exhibits a high recombination coefficient and low energy accommodation. Molecules desorbed from the surface may be expected to be vibrationally excited. A theoretical model based on the Eley–Rideal reaction mechanism [48] predicts the increase of $\gamma$ with wall temperature [49]. An experimental analysis of this phenomenon has been performed [20]. Figure 1 (taken from [20]) shows a decrease of relative density of hydrogen atoms as a function of the reactor external wall temperature, which could be explained by the variation of $\gamma$ [49]. by cooling the walls of the discharge chamber the hydrogen plasma dissociation degree is increased (as required, for example, for diamond synthesis in plasma) and, by contrast, the heating of the walls is used in order to decrease the H density (as required for negative ion volume sources) [4,20,46,47]. For example, an increase by a factor of seven in the yield of H atoms has been reached by cooling the microwave reactor walls [20]. An extended discussion of the dynamics of atom (molecule)–surface interactions is presented in the literature [50].

2.2. Hydrogen rovibrationally excited molecules

2.2.2.1. Diagnostics. Rotationally and vibrationally excited electronic ground state hydrogen molecules H$_2^-$ are thought to play a crucial role in the activation of a variety of elementary processes in the field of plasma chemistry (cf for example [51]). Examples include photo-dissociation dynamics [52], reactive scattering [53], surface reactions [10,37], and formation of H$^-$ ions.
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in plasmas [4, 34, 54]. The experimental techniques of coherent anti-Stokes Raman scattering (CARS) [12, 52], resonant-enhanced multi-photon ionization (REMPI) [10, 37], laser induced fluorescence (LIF) [55], or VUV laser absorption spectroscopy [11] are used to measure in situ the rovibrational distribution of H₂. Based on experimental data and kinetic modelling the following mechanisms for the rovibrational excitation of H₂ in ionizing plasma have been identified:

- resonant excitation via low-energy (≤ 10 eV) electron impact [56];
- excitation by electron impact (≥ 30 eV) of high lying electronic levels which radiatively decay to vibrationally excited states of the ground electronic state [57–59];
- neutralization of H₂⁺ and H₂⁺, which can occur in electron or negative ion collisions and on wall surfaces [69, 61];
- excitation in collisional recombinative desorption from the various surfaces [10, 37];
- excitation of adsorbed molecules by direct electron impact [62].

The important destruction processes of H₂⁺ are the following:

- collisional deactivation in gas phase [44, 63, 64];
- dissociative attachment [27–29];
- wall relaxation [60, 65].

Most of the experimental information available at the moment is about the gas phase processes of rovibrational excitation and deexcitation (cf for example [19]). At the same time less data are available about rovibrational molecular excitation on surfaces.

2.2.2. Modelling. As mentioned already, the chemical kinetic schemes of discharges in molecular gases have a limited accuracy without taking into consideration the form of the EEEDF in a plasma for ionization degrees less than ≈ 10⁻⁴. By now a number of schemes of calculation of the EEEDF in G₂ exist, but only in some of them [43–45] have the kinetics of free electrons been analysed together with the vibrational kinetics. On the other hand, it is known that a hydrogen plasma is characterized by an essential vibrational excitation of the molecules. Typical examples are negative ion sources [4, 10, 12] and atomic hydrogen sources [24], where the population of upper vibrational levels is controlled by the processes of radiative cascaded decay and recombination of the atoms respectively.

The effect of vibrational excitation on the EEDF is primarily determined by supersonic collisions, resulting in an increase of the electron energy and rate constants for the electron-neutral inelastic collisions [26, 44, 66]. This was demonstrated to be of importance in the vibrational excitation of molecular electronically excited states [25]. In a recently developed numerical scheme [45] along with the processes of vibrational (de-)excitation, the maximum complete set of electronic-vibrational bound-bound and bound-free transitions between the quantum states of H₂ have been taken into account. The electronic-vibrational transition probabilities (Franck-Condon factors and densities) were obtained by means of a numerical solution of Schrödinger equation for vibrational degrees of freedom of H₂.

Nowadays there is further experimental evidence that, besides the pure kinetic approach, the flow pattern of non-equilibrium hydrogen plasma is also essential to understand the plasma properties. The flow of wall stabilized plasmas in a cylindrical channel with axial gas flow has been considered [67]. The MHD conservation equations of energy and momentum, equation of continuity, the Maxwell equations and Ohm's law have been treated by the method described earlier [18]. It was shown that, in contrast to the noble gases or the nitrogen arc, in hydrogen a strongly constricted high-temperature axial channel is realized. Near the channel walls the hydrogen plasma ionization and dissociation degrees are sharply lower compared with the corresponding axial values. The reason for this is evident, i.e. for hydrogen the conductive heat flux to the walls of the channel exceeds the conductive heat flux in argon by more than an order of magnitude.

Combining the kinetic scheme with non-equilibrium chemical, vibrational and electronic particle interactions [45], the flow model [18, 67] would be an important step towards the creation of a full numerical model of non-equilibrium hydrogen plasma.

2.2.3. Surface excitation phenomena. Among the various gases hydrogen is the subject of special interest for heterogeneous catalysis, since it is very easily adsorbed by the surfaces and mainly in atomic form [48]. For the interaction of hydrogen with metal surfaces it has been reported in several papers, that translational and vibrational temperatures of molecules, leaving the surface after recombination of atomic hydrogen from the gas phase with the hydrogen atoms adsorbed on the surface, are much higher than those associated with surface temperature [10, 37, 68].
From the analysis of time-of-flight (TOF) spectra it has been shown [68], that hydrogen molecules desorbing from Cu have a very narrow velocity distribution, with a mean energy corresponding to a temperature four times larger than the surface temperature of the wall. These experimental results suggest that the hydrogen atoms permeating to the surface have a low probability to equilibrate in a chemisorption well. Moreover they rather equilibrate in a sub-surface well from where they recombine and desorb directly. The molecules resulting from the recombination of these atoms obtain their kinetic energy from the activation barrier for adsorption. The independent of the results on S and C coverage as well as on the crystallographic direction is a strong argument for the involved barrier being sub-surface.

The production of vibrationally excited hydrogen molecules (up to \(v = 9\)) have been demonstrated even in the absence of the discharge (see [37]). With the application of dissociative attachment of slow electrons to vibrationally excited molecules as a detection technique, it has been established [37] that the molecules are formed at recombinative desorption from the metal walls, with H atoms produced using a heated filament. The dynamics of the recombinative desorption process has been discussed [36] in the framework of the potential energy curve model of interactions of hydrogen with a metal surface. According to this scheme the atomic hydrogen has 2.24 eV available for recombination with an adsorbed atom with respect to the \(H_2\) molecular limit. Thus one would expect levels up to \(v = 4\) (1.88 eV) to be populated. Apparently higher lying levels are populated during \(V-V\) exchange processes [18]. Another possible explanation of the excess of energy, required for the population of high-lying vibrational states, is the existence of a weakly bound H state in the \(H_2-Cu\) potential energy surface. This explanation has been given in the literature [37, 69], and partially confirmed by Cacciatore et al [70]. However, it should be mentioned that in the experiment of Kubiak et al [71] on recombinative desorption of \(H_2\) from Cu surfaces, only the \(v = 1\) vibrational state has been detected and the mechanism proposed was of the Langmuir–Hinselwood type.

By using a REMPI technique the formation of vibrational highly excited molecules, up to \(v = 5\), by recombination of atoms on a cold metal surface was investigated [10]. About ten minutes elapsed after the discharge a heated element was shut off before production of vibrationally excited molecules via recombinative desorption took place. It was suggested [10] that this surface production mechanism would not be important in the presence of a discharge, because the necessary weakly bound hydrogen layer would be sputtered away. The delay between shut off the discharge and the \(H_2^*\) production suggests that surface conditions are changed by the discharge in some fashion which takes about ten minutes to recover.

The Eley–Rideal reaction mechanism for the recombinative desorption of hydrogen has been examined theoretically [69]. A two-dimensional model is used to describe the interaction between a gas phase atom and an atom bound to a metal surface, which combine to form a desorbing molecule. Large amounts of vibrational excitation are found, due to large exothermicity of the desorption process of \(H_2\). As an example, figure 2 taken from the literature [69], illustrates the vibrational populations of \(H_2\) molecules, desorbed from a copper and a tungsten surface, as a function of the kinetic energy of the incident atom. The calculated vibrational distributions are similar to those measured by Hall et al [37]: about 90% of the non-Boltzmann component of the vibrational populations is concentrated in about three neighbouring vibrational levels.

3. Hydrogen radicals in a recombining plasma

The analysis of ionizing plasma systems, carried out in the previous section, clearly shows that for the hydrogen radical kinetics both homogeneous processes in the gas phase, and heterogeneous processes on the surfaces are important. At the same time for the ionizing plasma one of the largest problems in determining the reaction paths consists of properly distinguishing between, followed by a separate analysis of, both homo- and heterogeneous reactions. To distinguish the gas phase and surface reactions the recombining plasma might be a promising candidate. In a recombining plasma, excitation through electron collisions is negligible as the electron temperature is rather small. Therefore the only mechanism that is capable of exciting the molecules is wall interaction.
The population density of atomic hydrogen in the first excited state $H^+(n = 2)$ in a freely expanding recombining hydrogen–argon plasma jet (cf figure 3) has been determined [72]. Using a kinetic model of the relevant atomic and molecular processes, which does not require information on the EEDF, the absolute density of atomic hydrogen in the ground state and the plasma dissociation degree from experimental data were derived. The dissociation degree in the expansion was less than 20% [22, 72]. At the same time the plasma source, a cascaded arc thermal plasma in pure hydrogen and in argon/hydrogen gas mixture was experimentally characterized by determination of the efficiency, the electric field, and the pressure gradient of the arc [73]. From the power balance measurements the hydrogen mass dissociation degree has been derived to be above 60%, which is much higher in comparison with less than 20% in the expansion of the arc [72]. The sharp decrease of the dissociation degree in the expansion leads to the hypothesis that hydrogen molecules must be created in the vessel through wall association of atoms, which together with a strong recirculation flow will provide a re-entry flow of $H_2$ into the plasma jet.

In previous works [74, 75] an expanding argon cascaded arc plasma with different amounts of hydrogen added was studied using optical emission spectroscopy, Langmuir probes and Thomson–Rayleigh scattering. The electron density and temperature, neutral particle density and excited hydrogen atoms $H^+(n \geq 3)$ absolute population density were determined as functions of the axial position in the expansion. The admixture of a small amount of hydrogen to the argon flow leads to a dramatic — up to four orders of magnitude — decrease of the charged particles density (cf figure 4, taken from [74]).

The explanation of this phenomena is the recirculation of wall associated $H_2$ in the vessel, which destructs the charged particle density by charge exchange to a molecular ion and subsequent dissociative recombination of the formed $ArH^+$ and $H_2^+$ molecular ions [74, 75]:

$$H^+[Ar^+] + H_2 \rightarrow H_2^+[ArH^+] + H \quad (1)$$

The charge exchange reaction (1) in pure hydrogen plasma will be exothermic, i.e. efficient, only if $H_2^+$ molecules will be rovibrationally excited with internal energy $\geq 1.9 \text{ eV}$.

The expanding plasma in nitrogen and an argon–nitrogen gas mixture has been analysed with the Langmuir probe and mass spectrometry diagnostics [76]. Figure 5 illustrates the radial plasma density profiles for nitrogen plasma at two axial positions. All plasma conditions were similar to the discussed argon–hydrogen case [74]. From a comparison of figures 4 and 5 it is clearly seen that the charged particle density in a pure hydrogen plasma is three orders of magnitude lower than in nitrogen plasmas. The charge transfer reaction $Ar^+ + H_2$ is approximately 20 times faster than the reaction $Ar^+ + N_2$ for temperatures in the range $T \approx 3000 \text{ K}$ [23]. The comparison of the rate constants for the charge transfer reaction between atomic ions and vibrationally non-excited molecules shows that the reaction $H^+ + H_2$ [77] is approximately ten times more effective than the rate constant for the reaction $N^+ + N_2$ [78]. This means that the difference in the rates of reaction (equation (1)) cannot explain a large difference in the plasma density for the hydrogen and nitrogen. Here it is very important to emphasise that the charge exchange reactions between the atomic ions and molecules will only be effective if the molecules ($H_2$ and $N_2$) are rovibrationally excited.

The qualitative analysis of hydrogen and nitrogen properties with respect to the gas phase vibrational excitation (see the data presented in table 1) and with
Figure 5. Radial ion density for nitrogen plasma at two axial positions marked on the figure. The arc current is 45 A and reactor pressure is 40 Pa, and the gas flow rate is 58 SCCm⁻¹ [76].

Table 1. Thresholds for reaction (1), $\Delta E_l$; rate constants for reaction (2) [30], $k_b$; and cross sections for the molecular vibrational excitation, $\sigma_{33}$ by direct electron impact $H_2(v=0) + e \rightarrow H_2(v=3) + e$ [79] for the $H_2$ and $N_2$ molecules.

<table>
<thead>
<tr>
<th></th>
<th>Hydrogen</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_l$ (eV)</td>
<td>1.83</td>
<td>1.03</td>
</tr>
<tr>
<td>$k_b$ (m⁻³ s⁻¹)</td>
<td>$2.3 \times 10^{18}(300/7)^{0.4}$</td>
<td>$1.8 \times 10^{18}(300/7)^{0.29}$</td>
</tr>
<tr>
<td>$\sigma_{33}$ (m⁻²)</td>
<td>$2 \times 10^{-23}$</td>
<td>$8 \times 10^{-21}$</td>
</tr>
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respect to the reactions (1) and (2) shows that, in general, a nitrogen plasma has a larger change to be vibrationally excited in the gas phase. Moreover, the rate for dissociative recombination is larger. Of course, due to the great variety of elementary processes involved, the vibrational kinetics of $H_2$ and $N_2$ are much more complicated than the description presented above. However, it is a generally accepted point of view that building up vibrational excitation of $N_2$ by gas phase reactions is much more favourable than for $H_2$ [80]. Since the vibrationally excited molecules play a crucial role in the plasma recombination, the explanation of the results, presented in figures 4 and 5 is put down to: (1) the origin of the source of $H_2^{\nu}$ and $N_2^{\nu}$ molecules and (2) the fact that $n_{H_2^{\nu}} > n_{N_2^{\nu}}$ in the expanding plasma.

The questions which arise are: what is the real difference between $H_2$ and $N_2$, and what is the additional source of $H_2^{\nu}$? Probably, the answer is in the diverse characteristics of hydrogen and nitrogen with respect to the adsorption/desorption mechanism on the walls. From surface chemistry it is known that hydrogen can be easily adsorbed by metal walls predominantly in atomic form. On the contrary, nitrogen is the last in a row among the atmospheric gases which adsorbs on metals [48, 81]. It has been stated [81] that at room temperature iron does not adsorb nitrogen at all. Therefore, this might be a reasonable explanation for the observed difference, since hydrogen molecules desorbing from the walls are highly rovibrationally excited [10, 37, 68, 69].

The absolute density of atomic hydrogen excited states in a magnetized expanding pure hydrogen plasma is measured using emission spectroscopy [32, 82]. In the experiments the cascaded arc has been operated under very low pressure of the order of 30 Torr, and very low hydrogen flow $\approx 8$ sec⁻¹. The motivation to apply a magnetic field and to use low pressure and gas flow is to avoid the observed strong recombination in a freely expanding plasma jet. in this case the cascaded arc plasma under investigation should be far from the thermal equilibrium [18]. The generated plasma beam will contain radicals and stable particles with a strong non-equilibrium characteristic of translational and internal degrees of freedom [67, 73]. In figure 6 the absolute population densities per statistical weight are shown as a function of the ionization potential of the levels. As is seen, in the expansion a population inversion is observed between the quantum states $3 < \nu < 7$. It is useful to express the hydrogen level population densities in terms of their deviation from the Saha-Boltzmann equilibrium, i.e. the so-called over- or underpopulation factor $b_\nu = n_\nu/n_\nu^{Saha}$ [83]. If a certain level $\nu$ is in equilibrium with the continuum, the $b_\nu$ value equals by definition the value of one [83]. Using $n_e$ and $T_e$ measured by a double Langmuir probe diagnostics, $b_\nu$ values corresponding to figure 6 are calculated. The result is shown in figure 7. Comparing the measured population densities with the densities calculated on basis of the measured $n_e$ and $T_e$, using a purely atomic collisional-radiative model, leads to the conclusion that purely atomic recombination processes cannot account for the large population densities observed [39]. It is
argued that molecular induced recombination reactions in which the negative ion participates should be taken into account:

$$\text{H}_2^+ [\text{H}^+] + \text{H}^- \rightarrow \text{H}_2[\text{H}] + \text{H}^+ (p).$$ (3)

Note that the reaction of mutual neutralization of H+ and H− can only lead to the excitation of the quantum states H(p ≤ 3).

Hydrogen negative ions H− and positive molecular ions H2+ are either generated by the arc or formed in the reactions with the participation of rovibrationally excited H2+ molecules, which are formed at the wall

$$\text{H}_2^+ + c \rightarrow \text{H}^- + \text{H}$$ (4)

$$\text{H}_2^+ + \text{H} \rightarrow \text{H}_2^+ + \text{H}.$$ (5)

Emission and absorption spectroscopy measurements of the Balmer line series of atomic hydrogen have been carried out in the cases of hydrocarbon (CH4 or C2H2) and silane (SiH4) injection in the early expansion of a pure argon cascaded arc plasma [84,85]. For such a design of the plasma source the combination of high densities and large flow velocities leads to a very high particle fluxes. Analysis of the emission spectra in the subsonic expansion shows that in most of the experimental conditions a relatively strong radiation of the Balmer lines takes place. Since the direct electronic excitation H(p ≥ 3) from the ground state is negligibly small [74,75], as Tc is low, the recombinative excitation of the excited levels has to be considered. Analysis of the kinetics and exothermicity of various reactions of recombination (direct dissociation of C2H2 and SiH4, dissociative recombination of ArH+ and H+ with electrons, mutual neutralisation of H+, H2+, H3+ with H−) clearly indicates that in the excitation of the quantum levels H(p ≥ 3) the rovibrationally excited hydrogen molecules H2+/H can play an important role as precursors of atomic lines excitation.

To avoid the influence of wall phenomena in the interpretation of charged particle recombination kinetics, a hydrogen microwave pulsed discharge freely localized in a space has been specially designed and investigated [86]. The temporal evolution of the charged particle density has been measured by the technique of absorption of a diagnostic microwave beam. The results show the fast exponential decay of electron density. It has been interpreted as a consequence of the fast dissociative recombination. Kinetic estimation show, that for this case the dissociative recombination of the complex molecular ions with the electrons are the main reasons for the plasma decay [86].

### 3.2. Modelling

The observation that the dissociation degree of hydrogen plasma drops in the expanding plasma [22,73,72] leads to the conclusion that the highly dissociated plasma flow is strongly mixed in the expansion vessel with the cold background gas. Since the molecular hydrogen flow from the arc is low, H2 must be created in the expansion vessel as a result of wall association. At the same time it is clear, that the crucial point of the kinetic schemes equations (1)–(5) is the presence in the recirculating plasma flow not simply H2(ν = 0), but rovibrationally excited hydrogen molecules H2+/H as well.

Such molecules might be generated in gas phase, but more probably on surface reactions of association of hydrogen atoms, followed by a desorption in the form of H2+/H. Experimental data on the properties of the desorbed molecules from the metal walls showed that H2 was highly vibrationally excited [10,37,68]. The reason is that the H atom has ΔE ≈ 2.24 eV available for the recombination with the surface H atom. The excess energy must be distributed between translation and internal (rotational and vibrational) degrees of freedom of H2. This means that surface desorption of H2 might be an effective source of rovibrationally excited molecules. From the chemical point of view such a phenomena could be classified as heterogeneous catalysis in plasma.
4. Conclusions

The diagnostics and modelling of both ionizing and recombining hydrogen plasma systems have been presented. Both gas phase and surface reactions of hydrogen radicals — atoms and rovibrationally excited molecules — have been reviewed.

It has been shown that the presence of rovibrationally excited hydrogen molecules in recombining plasma strongly influences the kinetics and even the direction of the chemical reactions. The formation mechanisms of these excited molecules are subject of special interest. Both homo- and heterogeneous collisional processes should be analysed in that respect. For the volume production of $H_{2u}$, the reactions of stepwise electron excitation and mutual neutralization of the ions (reaction (3)) have been analysed as possible candidates.

For the expanding cascaded arc plasma the transport of rovibrationally excited molecules formed in the arc could also be important.

The inelastic collisional processes of plasma particles on surfaces, including radical adsorption and desorption, could be interpreted as a catalytic action of the surfaces to the extent that it leads to changing of the particle excitation. For the non-equilibrium hydrogen plasma a special interest represents the heterogeneous reactions of catalytic atom recombination. In that case the desorbed molecules with the large probability leave the surface with a substantial rotational and/or vibrational energy, which depends on the recombinatio-desorption mechanisms. By convective gas flows the desorbed rovibrationally excited molecules can be transported into the plasma jet and strongly influence the plasma properties (see reactions (1)–(5)). In contrast with ionizing plasma systems, where the electron excitation gas phase phenomena determine the plasma properties, the recombining plasma with cold electrons (where the excitation processes from the plasma volume are negligibly small) represents a special interest — the analysis of particle excitation by means of surface processes.

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