

Effects of adding hydrogen to an argon glow discharge: overview of relevant processes and some qualitative explanations

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An overview is given of the various processes which may occur in an argon–hydrogen glow discharge plasma, including the cross sections and rate coefficients compiled from the literature. Based on a simple balance equation, the dissociation degree of H₂ is estimated for typical GD-MS and GD-OES conditions. Further, the effects of H₂ molecules and H atoms on the argon analytical glow discharge are predicted, *i.e.*, a drop in argon ion (and maybe electron) density, a drop in argon metastable atom density and a change in the electron energy distribution function. Based on these predicted effects, we try to explain observed changes in analytical characteristics.

1 Introduction

In recent years, there has been an increased interest in the effects of adding hydrogen to an analytical glow discharge, both when operated for optical emission spectrometry and mass spectrometry. Bengtson and Hånström¹ have observed that small amounts of hydrogen (<0.1% partial pressure) added to an argon glow discharge can significantly alter the analyte emission yields. The effects appeared to be unique for each spectral line, *i.e.*, enhancement has been observed for certain lines but quenching was found for other lines of the same element. Moreover, the effects seemed to be similar when hydrogen was introduced in gaseous form and when it was sputtered from the sample. The results showed that ‘matrix’ correction algorithms for hydrogen will be needed for accurate quantification in the analysis of surface layers containing hydrogen.¹ Hodoroaba *et al.*² have investigated the effects of small amounts of hydrogen (up to 0.6% partial pressure) on the emission intensities of Ar I, Ar II, Cu I and Cu II lines. They also observed a different behavior for different lines: the Ar I line intensities decreased as a function of hydrogen concentration, but not all to the same extent; on the other hand, some Ar II line intensities also decreased, but others were unaffected or even increased slightly. Similarly, some Cu I lines decreased whereas others increased or passed over a maximum. Finally, the Cu II lines appeared to decrease, but not all to the same extent.²

For glow discharge mass spectrometry (GD-MS), Smithwick *et al.*³ have reported that a much better correlation could be reached between measured relative sensitivity factors (RSFs) and values calculated from an empirical equilibrium model when 1% hydrogen was added to the argon gas. No mechanism was proposed in their paper to explain the improved correlation, but the authors suggest that this strong correlation may have significant potential for quantitative analysis when the RSFs could be more accurately predicted (although it should be realized that the mass spectrum becomes more complicated because of metal hydride ion lines, which can lead to mass spectral interferences). The same experiment has been repeated in our group, and the results of Smithwick have been confirmed.⁴ Similarly, in ref. 5 a more or less linear relationship was found between experimental RSFs (on a logarithmic scale) and the first ionization potential of various elements, when

0.2% v/v of H₂ was added to the argon gas. The RSFs calculated in this way from the ionization potentials corresponded within a factor of about 1.35 to the measured RSFs.⁵

The effect of hydrogen in an argon glow discharge, and in other kinds of discharge plasmas, has also been investigated by other authors. In refs. 6–9 the addition of hydrogen was found to cause a lowering of the ionization in the discharge, and in the argon ion and electron concentrations. Different kinds of processes appear to be responsible for this lowering, depending on the discharge conditions. Indeed, in the expanding arc discharge plasma,⁸ the responsible process is a kind of charge transfer mechanism between Ar⁺ and H₂, followed by very efficient electron–ion recombination (see also below). In a fast flowing glow discharge, with gas mixing close to the ion exit in order not to disturb the discharge, a drop in intensity was found for all major ions, except for Cu⁺, which increased in abundance.⁹ The authors suggested that this was due to quenching of highly excited Ar states (as precursors for most ions in the spectrum) by H₂, down to Ar* (4s) levels, hereby preventing ionization of most species in the discharge, but significantly boosting the Penning ionization of Cu atoms.⁹ Finally, it is also well known that the sputter yields decrease upon addition of hydrogen to a pure argon glow discharge, at constant pressure and current, due to the lower mass of hydrogen; this also results in more hydrogen implantation in the metal surface.¹⁰

In this paper, we will try to give an overview of all possible reactions in an argon–hydrogen plasma based on literature data, with special interest in cross section data or rate coefficients. Based on these reactions, we will then try to present some qualitative explanations about the possible role of hydrogen species in the argon glow discharge used for GD-MS and GD-OES.

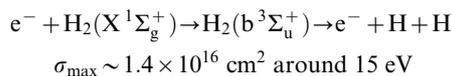
2 Overview of possible reactions in an argon–hydrogen glow discharge

An overview of the most important, inelastic processes between hydrogen species, argon species and electrons is presented in the appendix, with some indications about the cross sections (σ) or reaction rate coefficients (k).

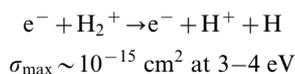
3 Estimation of the degree of dissociation of H₂ in an Ar–H₂ analytical glow discharge

From the reactions in the Appendix, a rough estimate will be made of the degree of dissociation of H₂ at typical GD-MS and GD-OES conditions. Looking at the cross sections of the reactions summarized in the Appendix, the most important production processes of H atoms are:

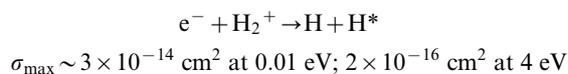
(1) Electron impact excitation of H₂ ground state to the triplet states, followed by radiative decay to the H₂ (*b* ³Σ_u⁺) state, and dissociation of the latter in two H atoms:



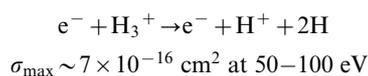
(2) Dissociative electron impact excitation of H₂⁺:



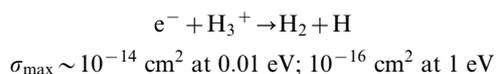
(3) Dissociative recombination between electrons and H₂⁺:



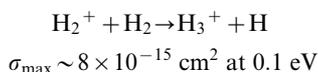
(4) Dissociative electron impact excitation of H₃⁺:



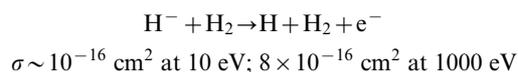
(5) Dissociative recombination between electrons and H₃⁺:



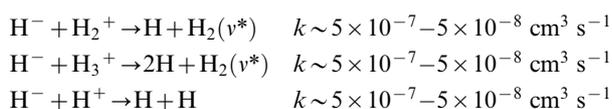
(6) Proton transfer between H₂ and H₂⁺:



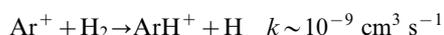
(7) One-electron stripping of H⁻ with H₂:



(8) Ion–ion recombination between H⁻ and H₂⁺, H₃⁺, H⁺:



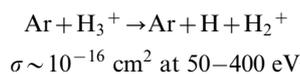
(9) Proton transfer between H₂ and Ar⁺:



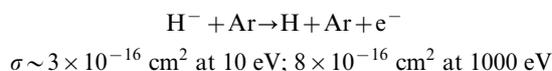
(10) Proton transfer between H₂⁺ and Ar:



(11) Collision-induced dissociation of H₃⁺ by Ar:



(12) One-electron stripping of H⁻ with Ar:



(13) Electron–ArH⁺ recombination:



Since the ionization cross sections for Ar→Ar⁺ and

H₂→H₂⁺ are of the same order of magnitude (*i.e.*, $\sim 10^{-16} \text{ cm}^2$), and since the Ar⁺:Ar density ratio is of the order of $10^{-4}\text{--}10^{-5}$, depending on the discharge conditions (*e.g.*, at 0.5–1 Torr, several mA: $n(\text{Ar}) \sim 10^{16} \text{ cm}^{-3}$, $n(\text{Ar}^+) \sim 10^{11}\text{--}10^{12} \text{ cm}^{-3}$, refs 11, 12; at 4 Torr, 30 mA: $n(\text{Ar}) \sim 10^{17} \text{ cm}^{-3}$, $n(\text{Ar}^+) \sim 10^{13} \text{ cm}^{-3}$, ref. 13), we expect that the density of the H₂⁺ ions is also several orders of magnitude lower than the H₂ density for the discharge conditions under study. Moreover, the major production process for H₃⁺ ions is the reaction between H₂ and H₂⁺ ions (proton transfer, see above). It appears even from model calculations for a hydrogen discharge that H₃⁺ is the dominant ionic hydrogen species, due to the rapid reaction of H₂⁺ ions with H₂.¹⁴ Hence, the H₃⁺ ion production will not be larger than the H₂⁺ ion production, and the sum of the H₂⁺ and H₃⁺ ion densities is expected to be several orders of magnitude lower than the H₂ density. Further, we assume that the H⁻ density is also much lower than the H₂ density. Since the cross sections for the reactions of the H-ionic species (H₂⁺, H₃⁺, H⁻) are not several orders of magnitude higher than the cross section for the H₂ reactions, we expect that only the latter will play a significant role in the production of H-atoms. This agrees with ref. 15, where it was reported that in a hydrogen microwave discharge about 90% of the H-atoms were created from H₂ molecules and only about 10% involved the molecular ion kinetics.¹⁵ Hence, this leaves us with reactions (1) and (9). Moreover, the ArH⁺ ions will rapidly react further with electrons, according to reaction (13), creating again a H-atom.

The dominant loss mechanism for the H-atoms is recombination with H-atoms at the walls. Indeed, the metallic walls are generally saturated with H-atoms, and they form the perfect surface for H-association and subsequent formation of H₂ molecules.⁸ The recombination factor, γ , is found to be around 0.1–0.25,^{16,17} depending on the kind of surface and wall material. Here we will assume a value of 0.2.

Based on this information, we can write a simplified balance equation for the production and loss of H-atoms:

$$\frac{\partial n_H}{\partial t} = n_{H_2} \times \left[\int_E F_e(E) \sigma_1(E) dE \times 2 + k_9 n_{Ar^+} \times 2 \right] - n_H \frac{D_{H-Ar}}{\Lambda^2} \gamma$$

The first two terms on the right-hand side correspond to the production of H-atoms, by reactions (1) and (9), respectively. $F_e(E)dE$ is the electron flux energy distribution function (in $\text{cm}^{-2} \text{ s}^{-1}$), $\sigma_1(E)$ is the cross section for reaction (1) (having a maximum of about $1.4 \times 10^{-16} \text{ cm}^2$ around 15 eV), k_9 is the rate coefficient for reaction 9 ($\sim 10^{-9} \text{ cm}^3 \text{ s}^{-1}$), and n_{Ar^+} is the argon ion density. The last term represents the loss of H-atoms due to diffusion and recombination at the walls. D_{H-Ar} is the H-atom diffusion coefficient in argon gas, calculated as follows for 1 Torr:¹⁸

$$D_{H-Ar} = \frac{1.0275 \times 10^4}{\left(\frac{d_H + d_{Ar}}{2}\right)^2} \sqrt{\frac{M_H + M_{Ar}}{2M_H \times M_{Ar}}}$$

where d and M are the atomic diameter and atomic mass, respectively. Inserting the appropriate values ($d_H = 3 \text{ \AA}$, $d_{Ar} = 3.64 \text{ \AA}$, $M_H = 1$, $M_{Ar} = 40$) yields $D_{H-Ar} = 667 \text{ cm}^2 \text{ s}^{-1}$ at 1 Torr and 300 K.

Finally, Λ is the characteristic diffusion length:¹⁹

$$\Lambda^2 = \frac{1}{\left(\frac{\pi}{L}\right)^2 + \left(\frac{2.4}{R}\right)^2}$$

where L and R are the length and radius of the (cylindrical) discharge cell.

Since the H-atom density is constant in time under steady-state conditions, the production and loss terms should be equal

to each other:

$$n_{\text{H}_2} \times \left[\int_E F_e(E) \sigma_1(E) dE \times 2 + k_9 n_{\text{Ar}^+} \times 2 \right] = n_{\text{H}} \frac{D_{\text{H-Ar}}}{A^2} \gamma \Rightarrow \frac{n_{\text{H}}}{n_{\text{H}_2}} = \frac{\int_E F_e(E) \sigma_1(E) dE \times 2 + k_9 n_{\text{Ar}^+} \times 2}{\frac{D_{\text{H-Ar}}}{A^2} \gamma} \quad (1)$$

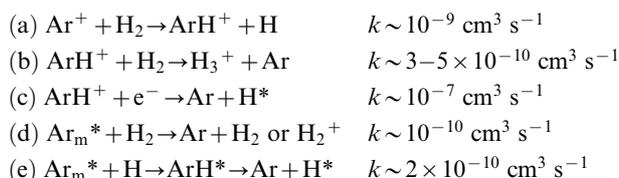
Estimated values for the quantities in the above equation are summarized in Table 1 for two different discharge conditions, typical for GD-MS (VG9000 cell) and for GD-OES (Grimm-type source). It follows then, from Table 1, that the estimated H:H₂ density ratio is about 5% for the GD-MS conditions (hence *ca.* 5% H and *ca.* 95% H₂), whereas for the GD-OES conditions a value of about 2 was calculated (hence *ca.* 67% H and *ca.* 33% H₂). The higher estimated value for the degree of dissociation for the GD-OES conditions is due to (i) the higher production of H-atoms (due to a higher argon ion density and electron flux energy distribution at higher discharge currents) and (ii) the lower diffusion coefficient at higher pressures, so that the H-atoms do not reach the walls so rapidly. It should, however, be realized that these values are only rough estimates, due to the simplified balance equation and the ‘order of magnitude’-values for the parameters in eqn. (1). In the near future, we plan to make a more detailed estimate, based on full modeling of the reaction processes and the various H-species. A number of such models, consisting of balance equations or Monte Carlo simulations for the various H-species, have been presented in the literature (*e.g.*, refs. 14, 20–24), but they apply to other plasma types than analytical glow discharges and to pure hydrogen.

Not much information can be found about degrees of dissociation in the literature. Moreover, most studies concerning hydrogen are generally applied to pure hydrogen discharges at completely different discharge conditions, and it is obvious that varying discharge conditions in an argon–hydrogen gas mixture will yield different results. In a pure hydrogen discharge operated in the radiofrequency mode, at conditions of about 40 Pa pressure and 110 W generator power, the degree of dissociation was observed to be about 1%, and this value barely changed when adding argon to the discharge.²⁵ In ref. 26, the dissociation fraction was calculated for a microwave discharge source at H₂ pressures in the range 0.02–1.5 Torr, and values of the order of 30–90% were obtained. In ref. 8 it was reported for the expanding cascaded arc plasma that the degree of dissociation was probably near 100%. However, during expansion of the arc, the H atoms will be able to reach the walls, giving rise to a ‘re-entry’ flow of H₂ molecules. It appears that these H₂ molecules are responsible for the observed effects of added hydrogen to the argon plasma.⁸ In ref. 27, the effect of argon on the dissociation rate of H₂ was

also studied, and it was found that the dissociation rate of H₂ in an argon–hydrogen glow discharge was much lower than in a pure hydrogen discharge. However, when looking at the results in more detail, it seems that the effect only becomes important for pressures above 5 Torr.²⁷

4 Effect of H and H₂ on the argon glow discharge

The degrees of dissociation estimated above can give us some insight into the effects of H-species in the argon glow discharge. We will consider only the processes between Ar-species and H-atoms or H₂ molecules, since the ionic H-species are assumed to be negligible compared with the atoms and molecules (see above). Based on the rate coefficients of the reactions summarized in the Appendix under A.4, it appears that the following reactions are dominant:



Reaction (a), followed rapidly by reaction (c) (see the high rate coefficient), results in a drop in both the Ar⁺ ion and electron densities. This was also the major conclusion for the cascaded arc plasma in ref. 8. For the GD-MS conditions, where we predicted a dominant contribution of H₂ molecules (see Table 1), the loss rate due to this mechanism is of the order of: $n(\text{Ar}^+) \times n(\text{H}_2) \times k \sim 10^{11} \times 10^{14} \times 10^{-9} \sim 10^{16} \text{ cm}^{-3} \text{ s}^{-1}$. Since the production of Ar⁺ ions and electrons by electron, ion and atom impact ionization is of the order of $1\text{--}7 \times 10^{16} \text{ cm}^{-3} \text{ s}^{-1}$ for the GD-MS conditions under study,¹¹ this loss mechanism will really play a role. For the GD-OES conditions, we estimated a much higher degree of dissociation. Nevertheless, it appeared from the reaction in Section 3 that exactly this process [reaction (a) followed by reaction (c)] is responsible for the dissociation of H₂ molecules, so that also for the GD-OES conditions, a drop in Ar⁺ ion and electron density is to be expected.

It should, however, be mentioned that the above reaction (a) can also be followed by reaction (b), as a competitor for reaction (c). Indeed, the rate coefficient for reaction (b) is about 2–3 orders of magnitude lower than for reaction (c), but the H₂ density is 2–3 orders of magnitude higher than the electron density (*cf.* Table 1, GD-MS conditions: $n(\text{H}_2) \sim 10^{14} \text{ cm}^{-3}$; $n_e \sim 10^{11} \text{ cm}^{-3}$ and GD-OES conditions: $n(\text{H}_2) \sim 10^{14}\text{--}10^{15} \text{ cm}^{-3}$; $n_e \sim 10^{13} \text{ cm}^{-3}$). Nevertheless, reaction (b) leads also to a loss of the Ar⁺ ions, and the H₃⁺ ions formed in reaction (b) react further (mainly with electrons, but also with H⁻ ions or Ar atoms) to yield H atoms (according to reactions (4), (5), (8)

Table 1 Typical values for the quantities in eqn. (1), for two different discharge conditions, typically used in GDMS and in GD-OES

Quantity	0.5 Torr, 1000 V, 3 mA, 300 K (values for VG9000 GDMS ¹¹)	4 Torr, 800 V, 30 mA, 500 K (values for Grimm GD-OES ¹³)
Ar ⁰ density	$\sim 10^{16} \text{ cm}^{-3}$	$\sim 10^{17} \text{ cm}^{-3}$
Ar ⁺ density	$\sim 10^{11} \text{ cm}^{-3}$	$\sim 10^{13} \text{ cm}^{-3}$
(H + H ₂) density (assumed 0.5% of Ar density)	$\sim 5 \times 10^{13} \text{ cm}^{-3}$	$\sim 5 \times 10^{14} \text{ cm}^{-3}$
$F_e(E)dE$ around 15 eV	$\sim 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$	$\sim 5 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$
$2 \times \int F_e(E)dE^* \sigma_1(E)$	$\sim 1\text{--}10 \text{ s}^{-1}$	$\sim 50\text{--}500 \text{ s}^{-1}$
$2 \times k_9 \times n_{\text{Ar}^+}$	$\sim 200 \text{ s}^{-1}$	$\sim 2 \times 10^4 \text{ s}^{-1}$
L	$\sim 1 \text{ cm}$	$\sim 8 \text{ cm}$
R	$\sim 1 \text{ cm}$	$\sim 0.2 \text{ cm}$
A^2	$\sim 0.064 \text{ cm}^2$	$\sim 0.00694 \text{ cm}^2$
$D(p, T)$	$\sim 1334 \text{ cm}^2 \text{ s}^{-1}$	$\sim 300 \text{ cm}^2 \text{ s}^{-1}$
$D \times \gamma / A^2$	$\sim 4200 \text{ s}^{-1}$	$\sim 8600 \text{ s}^{-1}$
$n_{\text{H}}/n_{\text{H}_2}$	$\sim 200/4200 \sim 0.048 = 5\%$	$\sim 2 \times 10^4/8600 \sim 2$
Hence: degree of dissociation	$\sim 5\% \text{ H}$	$\sim 67\%$

and (11), described in Section 3). Hence, reaction mechanism (b) also leads to a loss of Ar^+ ions and maybe electrons.

Further, the argon atoms in the 4s metastable levels ($^3\text{P}_2$ and $^3\text{P}_0$) appear to become de-excited (or quenched) by collisions with both H_2 molecules and H atoms, according to reactions (d) and (e), respectively. Indeed, for typical GD-MS conditions, the loss rate would be of the order of: $n(\text{Ar}_m^*) \times n(\text{H}_2) \times k \sim 10^{11} \times 10^{14} \times 10^{-10} \sim 10^{15} \text{ cm}^{-3} \text{ s}^{-1}$. This is also the order of magnitude of the typical production and loss processes of argon metastable atoms in a pure argon discharge,²⁸ so that quenching due to hydrogen is really expected to play a role. The same reasoning can be made for the typical GD-OES conditions (*i.e.*, loss rate $\sim n(\text{Ar}_m^*) \times n(\text{H}_2 + \text{H}) \times k \sim (10^{12} - 10^{13}) \times 10^{15} \times 10^{-10} \sim 10^{17} - 10^{18} \text{ cm}^{-3} \text{ s}^{-1}$). Hence, independently of the degree of dissociation of hydrogen in the discharge, the hydrogen-species seem to cause a drop in the argon metastable density.

Finally, it has been observed that adding H_2 to an argon discharge had a significant effect on the electron energy distribution function (EEDF).²⁹ Indeed, in an rf discharge at 40 Pa and 110 W in pure argon, the EEDF was Maxwell-distributed. When adding small fractions of H_2 (*e.g.*, 0.4%) to the discharge, electrons of 2–10 eV and above are easily consumed for vibrational and rotational excitations of H_2 , and the EEDF shifts to lower energies.²⁹ At *ca.* 2.8% H_2 , the EEDF is very similar to a pure H_2 discharge, with a severe depletion of high energy electrons compared with a Maxwell distribution.²⁹ It should, however, be mentioned that the effect of hydrogen on the EEDF strongly depends on the degree of dissociation of hydrogen. Indeed, H_2 strongly affects the EEDF, but H has only a minor influence. Hence, we expect that the EEDF will be mainly affected at low degrees of dissociation.

5 Implications of the effect of hydrogen on the analytical characteristics

From the point of view of basic plasma processes, the three major effects of hydrogen on an argon glow discharge are predicted to be: (i) a drop in Ar^+ ion and maybe also electron density (although possibly the electron density can increase due to other processes); (ii) a drop in argon metastable atom density; and (iii) a shift of the EEDF to lower energies. Because of the simplifications in the estimations (*i.e.*, many processes neglected, uncertainties in the cross sections and simplified balance equation) these predictions need to be checked by experiment for analytical glow discharges. However, we can already try to make an estimate of the implications of these effects of hydrogen on the analytical characteristics.

For GD-MS conditions, it is observed that the RSFs calculated with a simple empirical equilibrium model are in good agreement with the measured values,^{3,4} and also that the logarithms of the measured RSFs depend linearly on the ionization potentials.⁵ This can be explained by the drop in both Ar^+ ion and argon metastable densities. Indeed, the ionization of sputtered, analytically important, atoms in glow discharges is caused by Penning ionization (due to argon metastable atoms), asymmetric charge transfer with argon ions (although this process is rather selective, and does not occur for all atoms³⁰) and electron impact ionization, probably in decreasing order of importance.²⁸ When adding hydrogen to the argon discharge, both the Ar^+ ion and argon metastable atom density will drop, and hence asymmetric charge transfer and Penning ionization will become less important, in favor of electron impact ionization. The equilibrium model described in ref. 3 considers the equilibrium between electron impact ionization and recombination. Hence, this model can indeed be expected to give better results when electron impact ionization becomes the dominant ionization mechanism. Also the exponential dependence on the ionization potential

of the elements is expected to be better when electron impact ionization plays the dominant role. Indeed, this is the only ionization process which really correlates with the ionization potential, because Penning ionization always occurs, independently of the value of the ionization potential (as long as the latter is lower than the argon metastable energy), and the efficiency of asymmetric charge transfer depends on the availability of ionic energy levels lying close to the argon ion level. It should be mentioned that the ion peaks in the mass spectrum do not drop significantly in intensity⁴ (as would be expected when two important ionization pathways become less important). However, it can be argued that there would also be a drop in argon ion density and flux, resulting in a lower electrical current. Hence, since the measurements with and without hydrogen were performed at similar values of voltage and current,⁴ this could have been achieved by a higher pressure in the argon–hydrogen case, yielding more ionization. Unfortunately, this cannot really be checked, because the pressure cannot be measured in the standard VG9000 instrument. Harrison and co-workers,³¹ on the other hand, did observe a drop in analytical ion intensities when H_2O vapor was added to the discharge; this was explained by the lower sputtering rate of H-species and the quenching of argon metastable atoms, giving rise to less Penning ionization.³¹

For GD-OES, the effect of hydrogen is manifested in a change of optical emission intensities. However, it appears that when considering two lines of the same element (atomic or ionic), the one can increase and the other can decrease in intensity.^{1,2} This suggests that the effect of hydrogen, besides some general trends such as a drop in argon ion and argon metastable level populations and a change in the EEDF, can be rather selective, and is probably correlated to the energy of the excited levels (*e.g.*, quenching of some excited levels due to H atoms or H_2 molecules). This needs to be investigated in more detail by comparing the energy levels of the reacting species, and correlating this to the behavior of specific emission lines.

Finally, it should be mentioned that Bengtson and Hånström¹ observed the same effects on the emission intensities when H_2 gas was added to the discharge and when H-atoms coming from the sample entered the plasma. This is not surprising since both the conversion from H-atoms into H_2 molecules (due to wall association) and the reverse process (electron impact excitation, resulting in dissociation, or dissociative charge transfer with Ar^+ followed by electron–ion recombination) seem to occur at rather high rates. Hence, independently of the manner of introduction of H or H_2 to the discharge, an equilibrium will be established in the density ratio of H : H_2 , depending only on the discharge conditions and cell geometry (see Table 1).

6 Conclusion

It has been reported in the literature that the addition of hydrogen has a significant effect on the analytical characteristics of an argon glow discharge. In order to obtain a better insight into this behavior, we have made a compilation of all the processes occurring in an argon–hydrogen plasma. Based on the main processes, we have estimated the degree of dissociation of H_2 in an analytical glow discharge. It was found that at typical GD-MS conditions, the dissociation degree was about 5%, whereas for typical GD-OES conditions, a value of about 67% was estimated. It should, however, be mentioned that these predicted values are subject to considerable uncertainties, due to the various simplifications used for the estimation. In future work, we plan to develop a more detailed model, describing the behavior of various hydrogen species in a more complete way.

Based on the rate coefficients of the main reaction processes, we predicted further that the presence of H atoms and H_2

molecules will result in a drop in argon ion (and possibly electron) density, a drop in argon metastable atom density, and a shift of the EEDF towards lower energies. These effects have been correlated with the observed changes in analytical characteristics, *i.e.*, behavior of RSFs in GD-MS, and behavior of optical emission intensities in GD-OES, as a result of hydrogen addition.

To check the predictions made in this paper on the effect of hydrogen, more measurements have to be carried out: on the electrical current at constant pressure and voltage, on the argon ion, electron and argon metastable atom density, on the EEDF, and on the behavior of specific emission lines. Moreover, the degree of dissociation of hydrogen estimated in this work needs to be verified by more detailed modeling and by experiments (*e.g.*, by looking at H lines or H₂ bands in the emission spectrum).

Acknowledgements

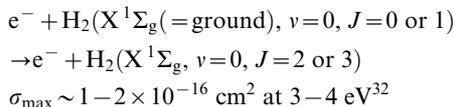
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Appendix: Overview of possible reactions in an argon–hydrogen glow discharge

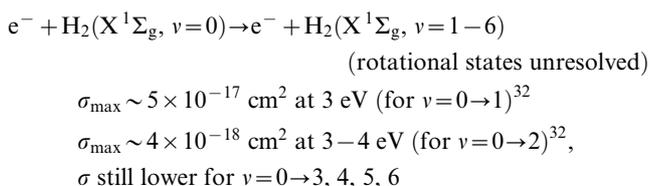
A.1 Reactions of electrons with hydrogen species or argon

(a) Electrons + H₂.

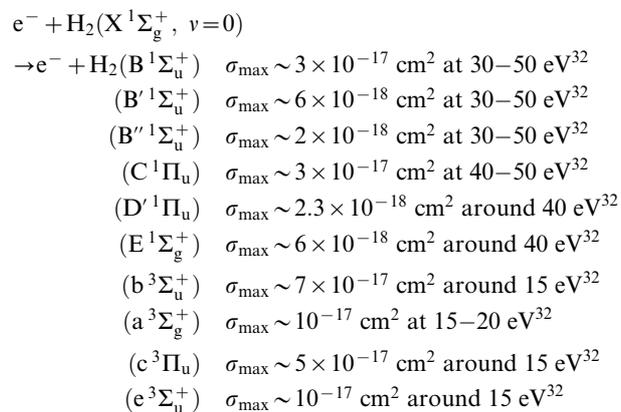
Rotational excitation.



Vibrational excitation.



Electronic excitation.



The singlet excited states radiate to the H₂(X¹Σ_g⁺) ground

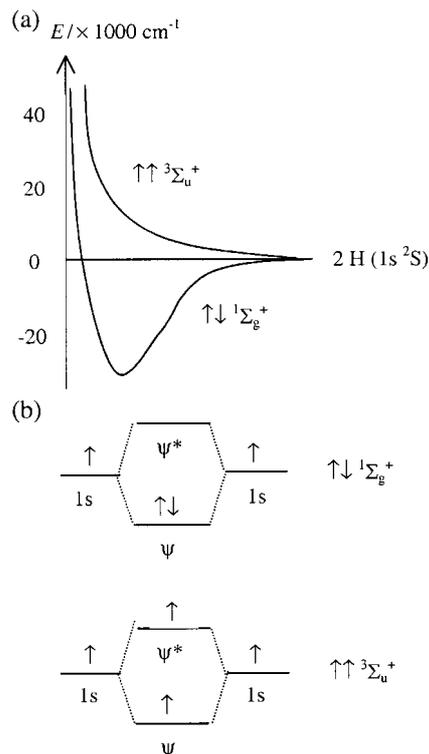
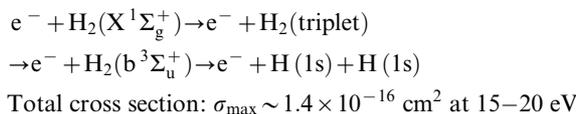
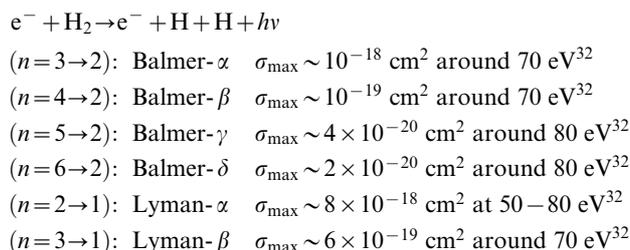


Fig. 1 Formation of a H₂ molecule in a stable (X¹Σ_g⁺) and a repulsive (b³Σ_u⁺) state, from two ground state H (1s) atoms. (a) Potential curves, (b) positioning of the two electrons in a binding (ψ) or anti-binding (ψ*) orbital.

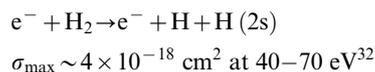
state.³³ The triplet states radiate to the second lowest H₂(b³Σ_u⁺) state,³³ also created from two H ground state atoms, but with one electron in an antibonding orbital (see Fig. 1). This state is repulsive, and will consequently dissociate into two H atoms. Hence:



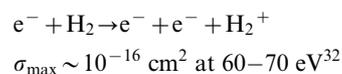
Dissociative excitation, followed by emission of radiation.



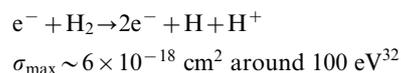
Dissociative excitation into metastable H (2s).



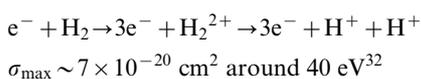
Ionization.



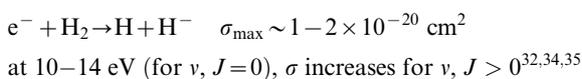
Dissociative ionization.



Dissociative double ionization.

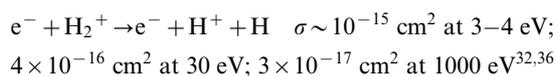


Dissociative attachment.

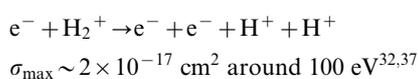


(b) Electrons + H₂⁺.

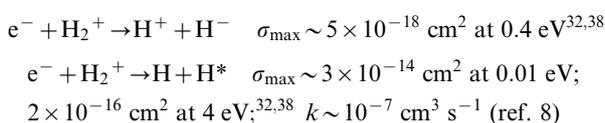
Dissociative excitation.



Dissociative ionization.

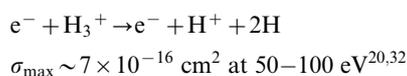


Dissociative recombination.

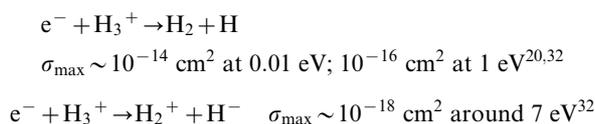


(c) Electrons + H₃⁺.

Dissociative excitation.

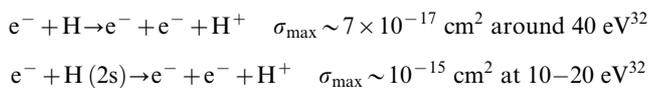


Dissociative recombination.

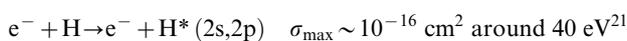


(d) Electrons + H.

Ionization.

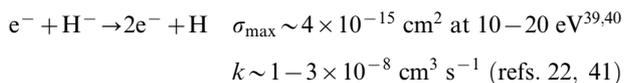


Excitation.



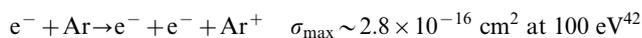
(e) Electrons + H⁻.

Electron detachment.

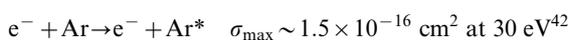


(f) Electrons + Ar.

Ionization.



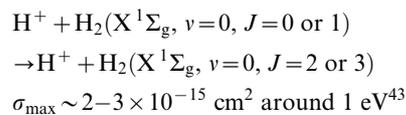
Total excitation.



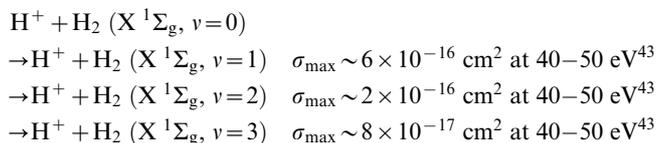
A.2 Reactions of hydrogen species with H₂

(g) H⁺ + H₂.

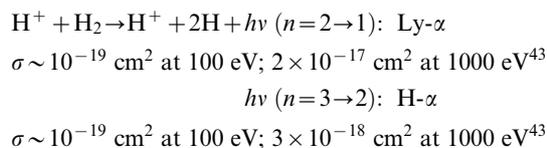
Rotational excitation.



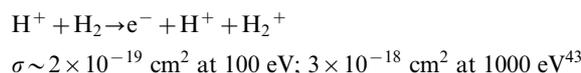
Vibrational excitation.



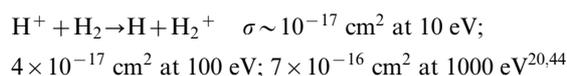
Dissociative excitation, followed by emission of radiation.



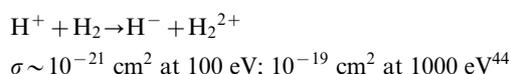
Ionization.



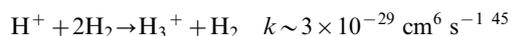
Charge transfer (one-electron capture).



Two-electron capture.

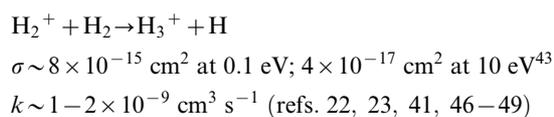


Proton capture.

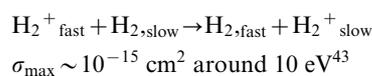


(h) H₂⁺ + H₂.

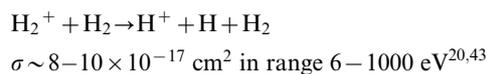
Proton transfer.



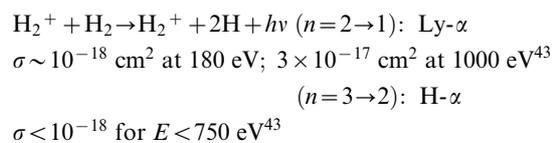
Charge transfer.



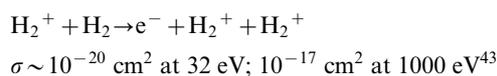
Dissociation.

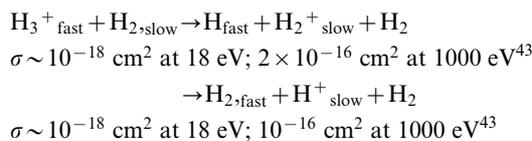
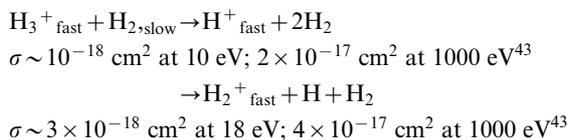
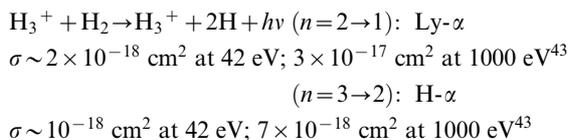
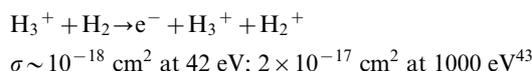
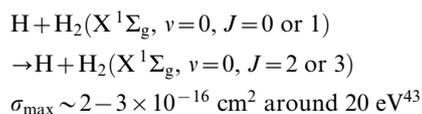
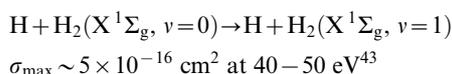
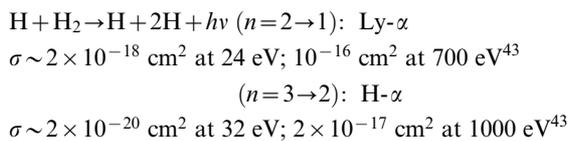
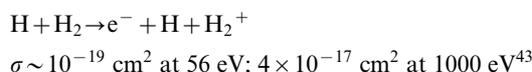
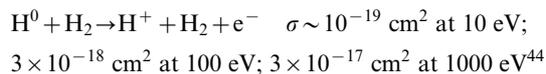
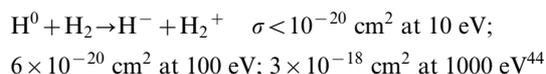
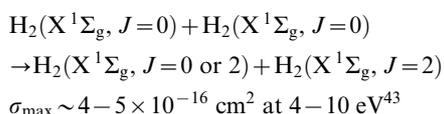
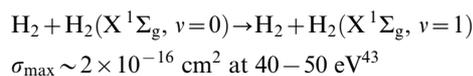
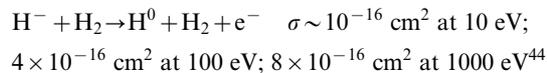
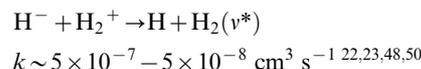
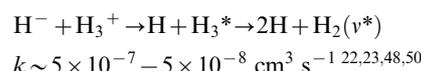
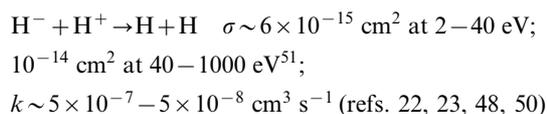
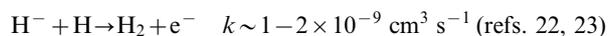
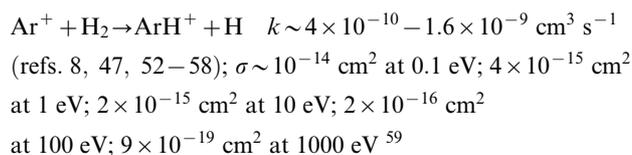
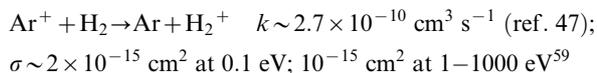
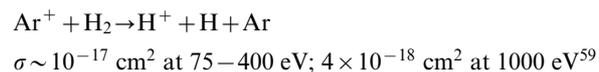
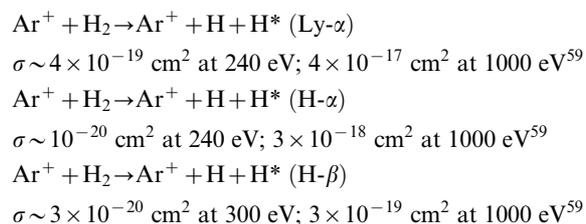


Dissociative excitation, followed by emission of radiation.



Ionization.



(i) H₃⁺ + H₂.*Charge transfer.**Dissociation.**Dissociative excitation, followed by emission of radiation.**Ionization.***(j) H + H₂.***Rotational excitation.**Vibrational excitation.**Dissociative excitation, followed by emission of radiation.**Ionization.**One-electron stripping.**One-electron capture.***(k) H₂ + H₂.***Rotational excitation.**Vibrational excitation.***(l) H⁻ + H₂.***One-electron stripping.**Two-electron stripping.***A.3 Reactions of H⁻ with other hydrogen species****(m) H⁻ + H₂⁺.***Ion-ion recombination.***(n) H⁻ + H₃⁺.***Ion-ion recombination.***(o) H⁻ + H⁺.***Ion-ion recombination.***(p) H⁻ + H.***Association.***A.4 Reactions of argon species with hydrogen species****(q) Ar⁺ + H₂.***Proton transfer.**Charge transfer.**Charge transfer, followed by dissociation.**Excitation.*

(r) Ar+H₂⁺.*Proton transfer.*

$$\text{Ar} + \text{H}_2^+ \rightarrow \text{ArH}^+ + \text{H} \quad k \sim 2.3 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \text{ (ref. 47)}$$

$$\sigma \sim 6 \times 10^{-15} \text{ cm}^2 \text{ (0.1 eV); } 2 \times 10^{-15} \text{ cm}^2 \text{ (1 eV);}$$

$$3 \times 10^{-16} \text{ cm}^2 \text{ (10 eV); } < 10^{-17} \text{ cm}^2 \text{ (} E > 20 \text{ eV)}^{59}$$

Charge transfer.

$$\text{Ar} + \text{H}_2^+ \rightarrow \text{Ar}^+ + \text{H}_2 \quad \sigma \sim 8 \times 10^{-16} \text{ cm}^2 \text{ (0.1 eV);}$$

$$3 \times 10^{-16} \text{ cm}^2 \text{ (1 eV); } 5 \times 10^{-16} \text{ cm}^2 \text{ (10 eV);}$$

$$10^{-15} \text{ cm}^2 \text{ (100–1000 eV)}^{59}$$

Dissociation.

$$\text{Ar} + \text{H}_2^+ \rightarrow \text{H}^+ + \text{H} + \text{Ar}$$

$$\sigma \sim 10^{-17} \text{ cm}^2 \text{ at 3 eV; } 6 \times 10^{-17} \text{ cm}^2 \text{ at 10–100 eV;}$$

$$8 \times 10^{-17} \text{ cm}^2 \text{ at 1000 eV}^{59}$$

Ionization.

$$\text{Ar} + \text{H}_2^+ \rightarrow \text{H}_2^+ + \text{Ar}^+ + \text{e}^-$$

$$\sigma \sim 10^{-17} \text{ cm}^2 \text{ at 240 eV; } 5 \times 10^{-17} \text{ cm}^2 \text{ at 1000 eV}^{59}$$

(s) Ar+H⁺.*Charge transfer (one-electron capture).*

$$\text{H}^+ + \text{Ar} \rightarrow \text{H}^0 + \text{Ar}^+$$

$$\sigma < 10^{-19} \text{ cm}^2 \text{ at } E < 50 \text{ eV; } 7 \times 10^{-18} \text{ cm}^2 \text{ at 100 eV;}$$

$$10^{-16} \text{ cm}^2 \text{ at 230 eV; } 10^{-15} \text{ cm}^2 \text{ at 1000 eV}^{59}$$

Two-electron capture.

$$\text{H}^+ + \text{Ar} \rightarrow \text{H}^- + \text{Ar}^{2+}$$

$$\sigma \sim 10^{-21} \text{ cm}^2 \text{ at 100 eV; } 7 \times 10^{-19} \text{ cm}^2 \text{ at 1000 eV}^{44}$$

Ionization.

$$\text{H}^+ + \text{Ar} \rightarrow \text{H}^+ + \text{Ar}^+ + \text{e}^-$$

$$\sigma < 10^{-19} \text{ cm}^2 \text{ at } E < 20 \text{ eV; } 5 \times 10^{-18} \text{ cm}^2 \text{ at 100 eV;}$$

$$10^{-17} \text{ cm}^2 \text{ at 230 eV; } 4 \times 10^{-17} \text{ cm}^2 \text{ at 1000 eV}^{59}$$

(t) Ar+H₃⁺.*Proton transfer.*

$$\text{Ar} + \text{H}_3^+ \rightarrow \text{ArH}^+ + \text{H}_2 \quad \sigma \sim 5 \times 10^{-16} \text{ cm}^2 \text{ at 1 eV;}$$

$$10^{-16} \text{ cm}^2 \text{ at 10 eV; } 10^{-18} \text{ cm}^2 \text{ at 32 eV}^{59}$$

Charge transfer followed by dissociation.

$$\text{Ar} + \text{H}_3^+ \rightarrow \text{Ar}^+ + \text{H} + \text{H}_2$$

$$\sigma \sim 10^{-18} \text{ cm}^2 \text{ at 1.3 eV; } 3 \times 10^{-16} \text{ cm}^2 \text{ at 4–1000 eV}^{59}$$

Collision-induced dissociation.

$$\text{Ar} + \text{H}_3^+ \rightarrow \text{H}^+ + \text{H}_2 + \text{Ar}$$

$$\sigma \sim 2\text{--}3 \times 10^{-16} \text{ cm}^2 \text{ at 50–400 eV}^{60}$$

$$\text{Ar} + \text{H}_3^+ \rightarrow \text{H} + \text{H}_2^+ + \text{Ar}$$

$$\sigma \sim 10^{-16} \text{ cm}^2 \text{ at 50–400 eV}^{60}$$

Ionization.

$$\text{Ar} + \text{H}_3^+ \rightarrow \text{Ar}^+ + \text{H}_3^+ + \text{e}^- \quad \sigma \sim 8 \times 10^{-19} \text{ cm}^2 \text{ at 13 eV;}$$

$$2 \times 10^{-17} \text{ cm}^2 \text{ at 100 eV; } 10^{-16} \text{ cm}^2 \text{ at 1000 eV}^{59}$$

(u) Ar+H⁰.*One-electron stripping.*

$$\text{H}^0 + \text{Ar} \rightarrow \text{H}^+ + \text{Ar}^0 + \text{e}^- \quad \sigma \sim 10^{-19} \text{ cm}^2 \text{ at 10 eV;}$$

$$10^{-17} \text{ cm}^2 \text{ at 100 eV; } 10^{-16} \text{ cm}^2 \text{ at 1000 eV}^{44,59}$$

One-electron capture.

$$\text{H}^0 + \text{Ar} \rightarrow \text{H}^- + \text{Ar}^+ \quad \sigma \sim 10^{-20} \text{ cm}^2 \text{ at 18 eV;}$$

$$3 \times 10^{-18} \text{ cm}^2 \text{ at 100–1000 eV}^{44,59}$$

Ionization.

$$\text{H}^0 + \text{Ar} \rightarrow \text{H} + \text{Ar}^+ + \text{e}^- \quad \sigma \sim 10^{-19} \text{ cm}^2 \text{ at 75 eV;}$$

$$4 \times 10^{-17} \text{ cm}^2 \text{ at 1000 eV}^{59}$$

Excitation.

$$\text{Ar} + \text{H}^0 \rightarrow \text{Ar} + \text{H}^* \text{ (Ly-}\alpha\text{)} \quad \sigma \sim 2 \times 10^{-20} \text{ cm}^2 \text{ at 13 eV;}$$

$$10^{-16} \text{ cm}^2 \text{ at 100–1000 eV}^{59}$$

$$\text{Ar} + \text{H}^0 \rightarrow \text{Ar} + \text{H}^* \text{ (H-}\alpha\text{)} \quad \sigma \sim 2 \times 10^{-20} \text{ cm}^2 \text{ (13 eV);}$$

$$7 \times 10^{-17} \text{ cm}^2 \text{ (100 eV); } 3 \times 10^{-17} \text{ cm}^2 \text{ (1000 eV)}^{59}$$

(v) Ar+H⁻.*One-electron stripping.*

$$\text{H}^- + \text{Ar} \rightarrow \text{H}^0 + \text{Ar} + \text{e}^- \quad \sigma \sim 3 \times 10^{-16} \text{ cm}^2 \text{ at 10 eV;}$$

$$5 \times 10^{-16} \text{ cm}^2 \text{ at 100 eV; } 8 \times 10^{-16} \text{ cm}^2 \text{ at 1000 eV}^{44,59}$$

Two-electron stripping.

$$\text{H}^- + \text{Ar} \rightarrow \text{H}^+ + \text{Ar} + 2\text{e}^- \quad \sigma \sim 10^{-19} \text{ cm}^2 \text{ at 18 eV;}$$

$$2 \times 10^{-18} \text{ cm}^2 \text{ at 100 eV; } 10^{-17} \text{ cm}^2 \text{ at 1000 eV}^{44,59}$$

Excitation.

$$\text{H}^- + \text{Ar} \rightarrow \text{H}^* \text{ (2s,2p)} + \text{e}^- + \text{Ar} \quad \sigma \sim 10^{-19} \text{ cm}^2 \text{ at 42 eV;}$$

$$2 \times 10^{-18} \text{ cm}^2 \text{ at 100 eV; } 7 \times 10^{-17} \text{ cm}^2 \text{ at 1000 eV}^{59}$$

(w) Ar+H₂.*Excitation.*

$$\text{Ar} + \text{H}_2 \rightarrow \text{Ar} + \text{H} + \text{H}^* \text{ (H-}\alpha\text{)} \quad \sigma \sim 5 \times 10^{-21} \text{ cm}^2 \text{ at 18 eV;}$$

$$4 \times 10^{-18} \text{ cm}^2 \text{ at 100–1000 eV}^{59}$$

$$\text{Ar} + \text{H}_2 \rightarrow \text{Ar} + \text{H} + \text{H}^* \text{ (H-}\beta\text{)} \quad \sigma \sim 10^{-20} \text{ cm}^2 \text{ (24 eV);}$$

$$10^{-18} \text{ cm}^2 \text{ (100 eV); } 5 \times 10^{-19} \text{ cm}^2 \text{ (1000 eV)}^{59}$$

(x) ArH⁺+H₂.*Proton transfer.*

$$\text{ArH}^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{Ar}$$

$$k \sim 3\text{--}5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ (refs. 47, 55, 59)}$$

(y) ArH⁺+e⁻.*Recombination.*

$$\text{ArH}^+ + \text{e}^- \rightarrow \text{Ar} + \text{H}^* \quad k \sim 10^{-7} \text{ cm}^3 \text{ s}^{-1} \text{ (ref. 8)}$$

(z) Ar_m^{*}+H₂.*Quenching.*

$$\text{Ar}_m^* \text{ (} ^3\text{P}_1\text{)} + \text{H}_2 \rightarrow \text{H}_2 + \text{Ar} \quad k = 7 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ (for } ^3\text{P}_2\text{);}$$

$$k = 8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \text{ (for } ^3\text{P}_0\text{)}^{61}$$

Penning ionization.

$$\text{Ar}_m^* + \text{H}_2 \rightarrow \text{H}_2^+ + \text{Ar} + \text{e}^- \quad k \sim 10^{-10} \text{ cm}^3 \text{ s}^{-1} \text{ (ref. 62)}$$

(aa) Ar_m* + H.
Excitation of H.

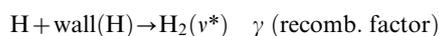


$$k = 2.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (\text{for } ^3\text{P}_2);$$

$$k = 2.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \quad (\text{for } ^3\text{P}_0)^{29,63,64}$$

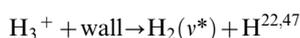
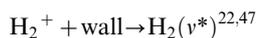
A.5 Effect of the walls

Recombinative desorption.



$$\sim 0.1 - 0.25 \text{ for most metal surfaces}^{16,17,39}$$

Ion neutralization.



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