Processes with neutral hydrogen and deuterium molecules relevant to edge plasma in tokamaks

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Abstract. Neutral hydrogen molecule is an important constituent of edge plasma in tokamak reactors. These molecules are continuously produced by ion neutralisation and recombination on plasma walls and are subsequently reemitted in the plasma. We initiated an experimental program to study processes in which vibrationally excited hydrogen molecules are involved. Two specific experimental techniques have been developed, one for vibrational spectroscopy of hydrogen molecules (H₂ and D₂) and another one for H and D depth profiling in materials. New information has been acquired on hydrogen recombination on tungsten and also on dissociative electron attachment in hydrogen, both relevant to edge plasma. Experimental set-ups are shortly presented as well as some of the results on above processes.

1. Introduction
Detailed understanding and characterization of plasma-wall interaction and edge plasma in present tokamaks and future fusion reactors is becoming more and more important due to the ITER project. Different atomic and molecular collision processes decisively determine various processes of primary importance for stable and reliable operation of fusion reactor. Such processes are for instance, the physical and chemical sputtering of the wall material, fuel retention in the wall and its recycling, plasma detachment in tokamak divertor, photon emission from the edge plasma, mitigation of transient phenomena etc. An extensive overview of different aspects of plasma-wall interaction is given in [1].

Neutral hydrogen atoms and molecules are present in the edge plasma. They are continuously generated by ion recombination on the wall of the fusion reactor and on other plasma facing components and then reemitted to the plasma. They can be created also by volume recombination of ions and electrons in the relatively cold edge plasma. The interaction of excited neutral molecules with the walls and their importance for the edge plasma is still not well understood since there is not many experimental studies of relevant processes. Optical emission spectroscopy of edge plasma, especially from limiter and divertor regions, brought evidence of abundant presence of molecules and their involvement in volume processes. Direct correlation of the observed phenomena to the processes with neutrals is mainly possible by numerical simulations and very important activity exists in this field. As experimental results accumulate and numerical methods become more sophisticated also more processes have to be included in the models. For adequate data bases completion more experimental and theoretical works are needed.

We have constructed a set-up for vibrational spectroscopy of hydrogen molecules (H₂ and D₂) that is based on the properties of the dissociative electron attachment in hydrogen in order to facilitate dedicated experimental studies of processes with hydrogen molecules. For the same purpose we also
developed a technique for in-situ measurement of H and D concentration in materials. This is done by ion beam analytical method ERDA (Elastic Recoil Detection Analysis), utilizing 4.2 MeV probing beam of \(^7\text{Li}^{2+}\) ions. A short description of experimental techniques and results on production of vibrationally excited hydrogen molecules on tungsten and copper and on the edge plasma relevant process of dissociative electron attachment in hydrogen are presented.

2. **Molecules in the edge plasma of tokamaks**

Hydrogen molecules are the primary fusion fuel that is injected into the plasma chamber before or during discharge ignition and also during different ramp-up plasma scenarios. Plasma fuelling is partially accomplished also by hydrogen desorption from the plasma wall during initial pulse rise. The details of atomic and molecular processes in this, initial stage of plasma ignition have negligible importance for the subsequent characteristics of the plasma behaviour so that they are never treated by modelling in detail. In a very short time core plasma becomes fully ionized and besides ions of the basic fusion constituents, D\(^+\), T\(^+\) and He\(^{2+}\) only some multiply charged ions of impurities might be present. Any neutral particle that happens to enter core plasma (atoms used for plasma heating and current drive or for diagnostic purposes, fuel pellets or stray neutrals from edge plasma) is promptly ionized.

Contrary to the initial evolution of plasma discharge in tokamak, the detailed atomic and molecular processes are very important for plasma behaviour closer to the plasma wall. This is due to the lower plasma temperature in this region and also to more complex composition of the plasma. The most characteristic case of this situation are the regions where carbon is used as a plasma facing material and very reach plasma chemistry occurs in the near wall region. Chemical erosion and subsequent carbon re-deposition are strongly dependent on the different reactions among hydrogen and different hydrocarbon molecules.

Plasma behaviour is particularly sensitive to a large set of atomic and molecular processes in tokamak divertors. By means of magnetic field configuration plasma is there intentionally directed to the specially designed target plates and very high power load is produced. While the normal power load to the plasma wall in the main reactor is bellow and close to 1 MW/m\(^2\), in divertor this load often reaches over 30 MW/m\(^2\). Such high power has to be spread over larger surface in order to achieve sufficient life time of the wall components and prevent failure.

Plasma wall material has to fulfill very strict requirements. First, it must be able to sustain high power load varying from relatively moderate one on the main chamber wall to the extreme one on the divertor targets. On the other hand material must not be a source of impurity ions that would contaminate the core plasma. Next, very important criterion is that the material has low hydrogen uptake in order to keep total amount of retained tritium in fusion reactor below legal safety level as long as possible. Due to the above criteria the following choice of wall material for ITER has been made: the main wall of the plasma reactor will be made of beryllium, majority of the divertor will made of tungsten castellated structures and only the divertor target plates exposed to the highest power flux will be made of graphite (CFC – carbon fibre composite). On this way the best compromise for all requirements is achieved although numerous problems remain to be clarified – migration of materials, the role of the mixed compounds and layers to the lifetime of components, dust production etc.

Neutral molecules are present during discharge also in the surrounding region, outside the edge plasma but still inside the reactor vacuum vessel. While strong magnetic field holds core plasma strictly out of contact with materials and its configuration allows gradual decrease of plasma temperature to the cold plasma regime where it is in contact with limiting materials (PFC – plasma-facing components) there are still regions where quasi neutral gas cushion exists between this edge plasma and vacuum vessel wall. Such hidden regions are for instance gaps between different first wall construction elements and castellation in divertor target plates, hidden space bellow the divertor dome, pumping and gas injection ducts, diagnostic ports and similar. Here, the characteristics of atoms and molecules play role in additional energy transfer between edge plasma and vacuum vessel, and also in the fuelling and pumping conditions.
As stated above, the recombination of hydrogen ions on the plasma wall is the source of neutral molecules that are subsequently reemitted into the plasma. Neutral particles that are emitted to the plasma do not feel electric and magnetic fields and can penetrate in plasma depending on their ionization length. This is dependent on plasma density and temperature and also on the nature and internal excitation of the particle. Highly vibrationally excited molecule will most probably be dissociated to negative ion and atom and these fragments will subsequently be ionized by ion or electron collision. Contrary to this, a ground state hydrogen molecule will most probably be ionized by electron impact directly to positive ion.

Different individual processes involving neutral hydrogen molecules are important for edge plasma. These processes influence plasma behaviour on a complex way as they occur simultaneously and their relative importance depends on plasma and electron density, particle concentrations and temperatures and E and B field configuration. For properly taking into account individual cross section (CS) and reaction rate complex collisional-radiative models have to be employed. Many of recent developments of modeling codes (e.g. [2]) are based on the work of Sawada and Fujimoto [3]. For such codes to be efficient a detailed data bases are needed that contain reliable data on numerous individual process. Many such data do exist (e.g. see [4] for hydrogen data) but many are also missing especially for heavier hydrogen isotopologues (see Janev in [1]). Only very few data on reaction CSs and rate coefficients exist for vibrationally excited H$_2$ [5]. For heavier isotopologues the situation is even less favorable and much effort is needed to fill the gaps in the needed data sets.

3. Experimental techniques

In order to perform dedicated laboratory studies of processes with vibrationally excited hydrogen molecules we have developed and tested specific experimental techniques described in this section.

3.1. Vibrational spectroscopy of hydrogen molecules

Experimental method for vibrational spectroscopy that we employ in our studies is based on properties of the lowest energy dissociative electron attachment (DEA) in hydrogen (“4 eV process”) and it is described in detail elsewhere [6, 7]. It is based on a very strong rise of the cross section for DEA, e+AB → AB$^-$ → A$^-$+B with ro-vibrational excitation of hydrogen molecule in its ground electronic state. A and B stand for any of hydrogen isotopes, in our case H or D, as DEA has the same properties for all hydrogen isotopologues. Excited ro-vibrational states of the ground electronic state of hydrogen can not be detected by simple emission spectroscopy as radiative transition probabilities are extremely small.

There are three main DEA processes in the low incident electron energy range. The first process has threshold at 3.72 eV (“4eV process”) and proceeds through attractive potential of the lowest, X$^2\Sigma_u^+$ resonant H$_2^-$ state. The second process, between 5 and 13 eV, proceeds through the repulsive $^2\Sigma_g^+$ state and leads to higher kinetic energy fragments. Finally, the third process with the threshold at 13.92 eV (“14eV process”) proceeds through attractive resonant state of the $^2\Sigma_g^+$ symmetry that dissociates to H$^-$ (D$^-$) and electronically excited (n=2) H (D) atom.

We have built a new set-up with magnetically collimated electron beam and specially designed extraction system [8]. Schematically it is shown in figure 1. Negative hydrogen ions, H$^-$ or D$^-$ are created by DEA in the region where electron beam intercepts sample gas target. These ions are extracted from interaction region by combined action of a rather broad electrostatic field and homogeneous guiding magnetic field and a ribbon shaped ion beam is formed. Ions are then mass filtered by properly positioned narrow selection slits and detected by channel electron multiplier. Details of extraction electrode system, model simulations and experimental results obtained with new system are described in detail in [8].

In order to measure the vibrational distribution in the target gas one records a dependence of ion yield on electron beam energy in the energy region between 0.1 and 5 eV. Vibrational distribution is obtained from such experimental spectrum by deconvolution using recent theoretical cross sections for DEA in hydrogen [9]. This deconvolution is also described in detail in [8].
Particular convenience of the described vibrational spectrometer is that it also allows detection of atomic hydrogen (H or D) [8]. This is done by measuring the yield of $\text{H}^+$ (or $\text{D}^+$) for electron energy just above the ionization threshold for $\text{e}^+\text{H(D)} \rightarrow \text{H}^+(\text{D}^+) + 2\text{e}$. For switching from negative ion to positive ion mode one needs to change the polarity of extraction field, to reverse the direction of magnetic field and to change voltages on the channel electron multiplier.

![Figure 1. Schematic representation of the vibrational spectrometer. In the present experiment we can reliably deduce populations up to $v=8$ in H$_2$ and up to $v=12$ in D$_2$.](image1)

![Figure 2. Schematic representation of HEC used for in situ measurements of H and D concentration. Thin Al foils are used on the entrance and exit windows of HEC in order to prevent hydrogen from leaking to the vacuum chamber. Typical hydrogen pressure in the cell was in the µbar range. Al foil on the exit window together with a second one placed in front of the detector serve to absorb scattered incident Li ions and prevent them to reach the detector. The thickness of the absorber foil is determined so to efficiently stop Li ions but to allow H and D to pass.](image2)

3.2. Determination of H and D concentration in materials

In order to perform a more detailed characterization of the surfaces where studied reactions with hydrogen atoms and molecules occur and to facilitate the interpretation of experimental results we have developed a method for in situ measurement of hydrogen concentration depth profile. For this purpose we use Elastic Recoil Detection Analysis (ERDA), a well established analytical method with fast ions. For this we use collimated beam of 4.2 MeV $^7\text{Li}^{2+}$ ions that impinges on sample surface at small angle, 15°, and H and D ions that are knocked out from the sample are detected in forward direction, again at 15° with respect to the sample surface [10]. The depth variation of the absolute concentration of H and D in the sample is obtained by analysing energy spectrum of the ejected ions. This method is set at the ERDA/RBS experimental station on 2MV tandem accelerator at Jožef Stefan Institute.

In order to be able to follow the evolution of hydrogen concentration profiles simultaneously with exposing surface to the controlled hydrogen atmosphere a special hydrogen exposure cell (HEC) was constructed [11]. The following experimental parameters can be varied: hydrogen atmosphere (pressure and composition - H$_2$ or D$_2$ can be introduced or a mixture of two), temperatures of the sample and of the wall and most important a partial dissociation of hydrogen gas can be achieved by thermal dissociation of molecules on a resistively heated tungsten filament. The hydrogen exposure cell used for the in situ measurements of hydrogen is shown in figure 2.

3.3. Sources of particles

For our present laboratory experiments we need sources of particles that are diagnosed by the above described diagnostic techniques. For this we are mostly using sources of vibrationally excited hydrogen molecules that operate on a traditional way: hydrogen flows through a gas cell where hot tungsten filament is present so that partially dissociated neutral atmosphere is created. Free atoms then recombine on cooled wall of the cell and vibrationally excited molecules are created. Neutral
hydrogen gas that exits from such a cell contains ground state molecules, excited molecules and atoms. Detailed composition of the effusing gas depends on the cell geometry, dissociation filament temperature, temperature and composition of the recombining wall.

Test source (TS) used for the present studies of vibrational distribution of molecules created by atom recombination on metals and its position on the vibrational spectrometer (DTVE-B) is shown in figure 3. A disk of the studied material (25 mm dia.) is placed close (5 mm) and parallel to the exit orifice (6 mm dia.) so that recombination at the sample disk determines to a large extent the vibrational composition of the effusing gas. On this way, the vibrational relaxation due to wall and volume (lower density in front of the orifice) collisions is minimized. Sample disk is mounted on the cold finger cooled by a water flow and dissociation filament is placed around this cold finger behind the sample.

![Figure 3](image.png)

**Figure 3.** Test source used for the measurements of vibrational distribution of molecules produced by atom recombination (a) and detection geometry of test source (TS) as mounted on the body of the vibrational spectrometer (DTVE-B).

Another source of hot hydrogen molecules working on the same principle as TS but having different geometry was made for studies of influence of hot molecules injected into plasma on plasma emission. The same source was also used for the study of a possible role of vibrationally excited hydrogen molecules in chemical erosion of carbon films [12].

Yet another device that we are starting to use is a commercial source of atomic hydrogen HABS manufactured by MBE GmbH.

4. Results

4.1. Recombination of hydrogen atoms at metal surface

Production of hydrogen molecules by atom recombination at high-Z metal surfaces, tungsten in particular, has relevance to fusion development research because the largest part of divertor of ITER tokamak will be made of tungsten. Experiment with all-tungsten wall in Asdex Upgrade tokamak at Garching, also promoted the interest for all various reactions on tungsten. Reactions on some other high-Z materials such as Ta and Mo and also on Cu are also important to be studied due to other uses in reactors. Metal surfaces where reactions occur can be under very different conditions – from very high temperatures above melting point and under high plasma load and particle fluxes in the $10^{25}$ ions/m² range to rather low temperatures and shadowed from the direct plasma impact. Therefore detailed understanding of reactions on tungsten is very important and promptly needed.

4.1.1. Atom recombination at metal surfaces - hot atoms

Vibrationally excited molecules are produced by a recombination of hydrogen atoms on a surface that is exposed to the flow of hydrogen atoms. When the surface temperature is rather low (few °C) and atoms are impinging on the surface the mechanism of recombination is Eley-Rideal like. An incoming atom recombines with another atom adsorbed on the surface. There is another limiting recombination mechanism, Langimour-Hinshelwood, where two atoms adsorbed on the surface recombine and desorb as a molecule. The chemisorption energy ($E_{ch}$) of hydrogen atom adsorbed on a metallic
surface varies from 0.2 eV to 1 eV. Therefore when two chemisorbed atoms recombine they need to obtain the lacking energy from the surface and if the surface temperature is too low, the atoms cannot recombine. In the case of the Eley-Rideal mechanism the free atom brings 2.24 eV of potential energy (one half of the dissociation energy of hydrogen molecule) and molecule desorbes with a maximum available energy of \(2.24 \text{ eV} - E_{\text{ch}}\). Latest studies of interaction of H atoms with clean D covered metal surfaces have shown that the desorption rates of molecules are not Eley-Ridel like [13-15]. Beside that homonuclear products (D\(_2\)) were detected, which cannot be explained with the mechanism described above. This finding was explained by assuming a hot-atom mechanism [16-18]. A hot-atom concept is based on a fact that when an atom approaches the surface it gains considerable amount of energy (about 2.5 eV), due to the attractive potential between the atom and the metal. This energetic atom can then rather easily move along the surface, slowly giving its energy to the adsorbates and the substrate. This hot-atom can then either recombine with an adsorbed atom from the surface or stick to the surface by exchanging its energy with an adsorbed atom, creating another hot-atom. With the developed kinetic models [17, 18], the experimental desorption rates of HD and D\(_2\) were nicely reproduced. Still the developed models can explain only the formation of molecules with maximum energy of \(2.24 \text{ eV} - E_{\text{ch}}\) allowing the population of vibrational levels up to \(v=4\). Population of higher levels can then only be explained through recombination of two hot-atoms which are in the limiting case almost free with total available energy of about 2x2.24 eV. This high exceeding energy can then be transferred to the translational and internal degrees of freedom of the desorbing molecule formed by recombination. This could explain the population of vibrational states higher than \(v=4\). This process was neglected in the models due to the low-atom beam flux in treated experiments and expected rapid adsorbate relaxation [18]. New experiments are needed where recombination could be studied under higher atom flux and establish conditions where the recombination between two hot-atoms is possible.

4.1.2. Results

In order to study vibrational distribution of molecules created by surface recombination on metals we performed special dedicated experiments with the gas cell TS described above. Such geometry is used in order to enhance detection efficiency. Inconvenience of this method is that the vibrational distribution that is measured is not only a result of initial atom surface recombination but also of subsequent volume and wall collisions of created molecules. Therefore nascent vibrational distribution is necessarily modified to some extent depending on the geometry and the pressure in the cell. Comparing results with different sample materials allows one to estimate the contribution of secondary effects to the direct contribution from recombination on the sample.

A set of experimental measurements were performed recently using the TS with a 0.3 mm thick and 25 mm dia. disc sample made of tungsten (Goodfellow, hot rolled) [19]. Vibrational distributions for H\(_2\) (squares) and D\(_2\) (circles) molecules are shown in figure 4. Results are shown for two different kind of dissociation filaments, 0.2 mm dia. thoriated tungsten wire (labeled (1) in the figure) and 0.3 pure tungsten filament (labeled (2)). Two lines with different pre-exponential factors are also drawn in the figure, one corresponding to vibrational temperature \(T_v=3400\) K and another to \(T_v=3700\) K. As seen from the figure the lower temperature fits well vibrational distribution for D\(_2\) while the higher one fits well the distribution for H\(_2\).

Experimental distribution of H\(_2\) obtained on another, older experiment is also shown in figure 4. It was obtained from some previous measurements performed at the experiment in Paris described in details in [20]. Main difference between the two cases is the shape and conditions in the H\(_2\)(v) cell. In the old experiment tungsten was evaporated in-situ to the inner wall of the cell so that clean thin polycrystalline layer is deposited. In the present case we use commercial hot rolled tungsten conventionally polished and cleaned. Also, the pressure was higher in the old experiment (0.04 mbar) with respect to the present one (0.001 mbar). Besides these differences the vibrational distributions are similar but the older one is better described by lower vibrational temperature, \(T_v=3000\) K.

Vibrational distribution as obtained by recombination of hydrogen atoms on copper is shown in figure 5. Recombination disc for this experiment was made of commercial OFHC copper
In this case much lower vibrational temperature was obtained and as a consequence of this a very small production rate of D was measured. This effect clearly illustrates very big importance of material property on behavior of different hydrogen isotopologues in edge plasma.

Our present measurements in main points confirm previous findings for studied materials performed with H\textsubscript{2} [20] but extend the study to more fusion relevant D\textsubscript{2}. For both presented cases apparently lower vibrational temperature is obtained for D\textsubscript{2} than for H\textsubscript{2}. It is important to note that measured vibrational distributions are often not reproducible and that they also evolve with time. All this indicates that detailed conditions on the surface are very important for the process of atom recombination and therefore for the resulting vibrational distribution of reemitted molecules.

In order to improve our understanding of recombination process we have undertaken complementary studies with the same quality of tungsten by in-situ ERDA analysis of hydrogen concentration depth profile using HEC [11], [19]. Conditions in HEC are comparable and very similar to the surface exposure conditions in TS. The only important difference between HEC and H\textsubscript{2}(v) cells used for production of hot molecules is that the first one has quasi stationary gas atmosphere while for the later ones there is always an hydrogen flow through the cell. Other characteristics, apart from the geometry are the same – dissociation filament, partially dissociated hydrogen atmosphere, atom recombination on the sample surface.

![Figure 4](image1.png)  
**Figure 4.** Relative vibrational populations of H\textsubscript{2} and D\textsubscript{2} molecules formed by atom recombination on tungsten as a function of excitation energy. Positions of individual vibrational state for the two molecules are indicated in the figure.

![Figure 5](image2.png)  
**Figure 5.** Same as in figure 4 but for recombination of H and D atoms on copper.

Rather high initial H-concentration on the surface was measured (about 30\times10\textsuperscript{15} H-atoms/cm\textsuperscript{2}) which is at least three times higher than could be expected even for rough surface. As the sample was only conventionally cleaned it is apparent that impurities remained on the surface. When D\textsubscript{2} is introduced in HEC and dissociation filament is turned on an isotope exchange reaction occur. Due to the incertitude in absolute values of D concentration [11] we can not for the moment compare the absolute size of the steps in H (decrease) and D (increase) concentration time dependence. After some time D concentration becomes stationary but H concentration still remains rather high indicating that only a part of hydrogen on the surface was actively taking part in the exchange reaction. Apparently there are two kinds of hydrogen atoms on the surface, one is strongly bound in impurity compound and another one is more mobile and easily exchangeable with incoming D atoms. Slow decrease of H.
concentration after initial rapid exchange decrease is observed and this is presumably an indication of the cleaning action of D atoms of the impurity layer.

Above study shows how detailed information is needed in order to well understand and interpret observed vibrational distributions of molecules created at the surface by atom recombination. Detailed further study of these phenomena is under way by means of another experimental arrangement using in situ exposure of tungsten surface to the H (D) atom beam.

4.2. Dissociative electron attachment in hydrogen

Besides being an important atomic collision process for the edge plasma the DEA in hydrogen is a benchmark case for theoretical calculations of resonant processes in electron molecule scattering (e.g. [9]). However, surprisingly no absolute measurements were done since pioneering measurements of Rapp et al. [21] and Schulz and Asundi [22] in sixties. This is also valid for the study of spectacular dependence of cross sections for DEA in hydrogen on target ro-vibrational excitation that was performed only by Alan and Wong [23] in 1978. All modelling of plasmas where DEA is taken into account are performed by using theoretically calculated CSs. All experimental absolute CS values for the low energy, 4eV process are obtained by normalization to the absolute values of Rapp et al. [21].

Our present experimental set up is not intended for measurements of absolute CS and we rely on theoretical CSs from [9] when extracting vibrational distributions from H' and D' yields. However, detailed measurements with cold gas target allowed us to establish with high statistical weight the ratios between 14 eV and 4 eV processes in both H_2 and D_2. All measurements of H' and D' yields as a function of electron energy show an important signal background that starts at about 11 eV and whose relative intensity varies for different experimental arrangements used by different groups. We have shown by changing ion detection conditions that this background is not due to the negative ions from DEA but to some other particles reaching ion detector and inducing secondary electrons that are subsequently multiplied and detected as counts. These secondary particles are most probably metastable molecules produced by electron impact excitation of triplet states a^3\Sigma_g^+ and c^3\Pi_u of hydrogen. This is indicated by observed steep threshold rise of the background that is characteristic for excitation of triplet states and also by the energy position of background threshold being close to the threshold of the triplet excitation at 11.8 eV. At higher electron energy UV photons produced by electron impact excitation of the lowest singlet states in hydrogen can contribute to the background as well. Presence of this strong background, that is very strong in [21], is systematically neglected in literature and therefore we proposed revised set of values for the 14 eV DEA in H_2, HD and D_2 by subtracting the contribution of the background [24]. Background was determined by polynomial fit of the wings of published CS where 14 eV DEA can not contribute to the signal. A preliminary set of values for the 4 eV process was also presented [24] as obtained from the measurements of the ratio of H' and D' signal from two processes in H_2 and D_2 respectively. During recent work on vibrational spectrometer we have determined this ratio with higher statistical weight and can state that ratio of DEA CS for 14 eV process to the CS for the 4 eV process is 11.5±1.4 and 1040±120 for H_2 and D_2 respectively. The original 14 eV CS from [21], the corrected 14 eV CS and new experimental values for the 4 eV process obtained from CS ratios are presented in Table 1.
Table 1. Cross sections for dissociative electron attachment in hydrogen for 14 eV and 4 eV process for cold molecules

|        | DEA CS for 14 eV process Rapp et al. [21] [10^{-24} m^2] | DEA CS for 14 eV process [21] corrected for background [10^{-24} m^2] | DEA CS for 4 eV process – present result [10^{-26} m^2] |
|--------|--------------------------------------------------------|------------------------------------------------------------------|--------------------------------------------------------|
| H2     | 2.1                                                   | 1.6                                                              | 14                                                    |
| HD     | 1.5                                                   | 1.0                                                              | -                                                     |
| D2     | 1.0                                                   | 0.45                                                             | 0.043                                                 |

Strong isotope effect observed in DEA in hydrogen was first reported by Schulz and Asundi [22] and it is an important characteristic of this process. Calculated cross sections [9] reproduce observed strong decrease of CS with molecular mass and extrapolate this dependence also to heavier isotopologues. Isotope effect is illustrated by spectra of H/H2 and D/D2 shown in figure 6. For both cases background contribution to the signal is observed and it is relatively more important in the case of D2 as CS for DEA is smaller while the CS for electronic excitation producing the background is approximately the same.

![Figure 6](image.png)

Figure 6. Experimental spectra for DEA to cold molecules for H2 and D2. Positions of different thresholds are also indicated in the figures.

Even though the CS for the 4 eV DEA process is negligible for heavy hydrogen isotopologues in the ground state the increase of CS with internal vibrational excitation is much faster for them so that for all hydrogen isotomomers CSs become very high, in the range of 10^{-15} cm^2 when excitation energy is above 2 eV. This property makes DEA in hydrogen very relevant for the edge plasma modelling if molecules are vibrationally excited.

5. Conclusions

New experimental techniques that have been recently developed in our laboratory are presented in this report. A short overlook of recent studies of vibrational distribution of molecules created by hydrogen atom recombination at metal surfaces is presented as well as measurements of H and D concentration on the surface of W. New evaluation of DEA CS is presented and new experimental values for 4eV process in H2 and D2 are given. Further work on these processes as well as on some other processes of relevance to fusion edge plasma are in progress.

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