Experimental Studies of Processes with Vibrationally Excited Hydrogen Molecules that are Important for Tokamak Edge Plasma

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ABSTRACT

We are currently conducting a series of different laboratory experimental studies of processes involving vibrationally excited hydrogen molecules that are relevant to fusion edge plasma. A general overview of our activities is presented together with results of studies of hydrogen recombination on surfaces. This includes vibrational spectroscopy of molecules formed by recombination on metal surfaces exposed to the partially dissociated hydrogen gas and recombination after hydrogen permeation through metal membrane. The goal of these studies is to provide numerical parameters needed for edge plasma modelling and better understanding of plasma wall interaction processes.

1 INTRODUCTION

Numerous atomic collision processes take place in the edge plasma of tokamak fusion reactors thus influencing both, stability of plasma discharge and plasma interaction with the wall and other plasma facing components. Neutral atoms, molecules and radicals are also present in the edge plasma together with electrons and ionized species. Complex interrelation of reactions among all these particles and also their interaction with the plasma wall determines the overall behaviour of edge plasma.

Neutral hydrogen molecules are one of very important constituents of the edge and divertor plasma. The main source of these molecules is the process of hydrogen recycling, driven by plasma neutralisation on the wall and subsequent hydrogen release. Neutral hydrogen molecules in the plasma edge and divertor are generally in excited vibrational states. Vibrational temperatures ranging from 3000 to 9000 K were measured in ASDEX Upgrade plasma [1] and rotational and vibrational hydrogen molecules were also studied in TEXTOR-94 [2]. Further spectroscopic studies of D2 were performed more recently in TEXTOR-94 [3] and DIII-D [4]. Molecules in edge plasma are especially important for the plasma detachment in divertor and importance of molecular excitation to corresponding processes is analysed (e.g. [5]). High importance of vibrationally excited hydrogen molecules has been recently recognised for direct plasma cooling in divertor plasma simulator PISCES-A [6]. Very detailed modelling of edge plasma is currently available [7] that takes into account all individual collision processes. Special databases have been established with critically evaluated and estimated cross sections and rate coefficients (e.g. [8]). Modelling codes now include also various photon induced processes and give more detailed insight into edge and divertor plasma conditions of ITER [9]. Recent modelling of divertor plasma show higher relative importance of neutral particles and also higher importance of volume, even three body processes with respect to the processes at the targets. However, in order to further
develop understanding of the phenomena in edge and divertor plasma one needs new imputs into the existing databases especially as the use of new wall materials such as Be are planned.

In order to elucidate some of the problems related to the role of vibrationally excited hydrogen molecules in the edge plasma and to contribute to the database we initiated systematic study of processes involving vibrationally excited hydrogen molecules that are relevant to edge plasma physics and plasma wall interaction [10] and here we present short overview of results.

2 EXPERIMENTAL METHOD

New experimental set-up and measurement procedures have been developed. The main experimental technique that we employ is vibrational spectroscopy of hydrogen molecules. The spectroscopy method is based on the properties of dissociative electron attachment to hydrogen molecules in electronic ground state through the lowest resonant state at around 4 eV. We have also developed hydrogen depth profiling in material because surface processes are of our main present interest. This is based on ion beam analytical method ERDA (Elastic Recoil Detection Analysis) where Li ions are used as a probing beam [11]. Specific experimental arrangements are used for studies of particular processes. Here we describe two such arrangements for studying hydrogen recombination at metal surfaces.

2.1 Hydrogen vibrational spectroscopy

Vibrational spectroscopy of hydrogen molecules ([12] and references therein) is based on the properties of dissociative electron attachment (DEA) \( e + H_2 \rightarrow H^- + H \). 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 a threshold at 13.92 eV (“14eV process”) proceeds through another attractive resonant state of the \( 2\Sigma_g^+ \) symmetry that dissociates to \( H^- \) and electronically excited \( n=2 \) \( H \) atom. For spectroscopic purpose we are mainly interested for 4eV process.

The method is based on the fact that by the lowest energy DEA in hydrogen "zero" energy ions are produced with high probability at the threshold. For the ground vibrational state \( v=0 \) this threshold is, according to the energy conservation, at \( E_{th} = D(H_2) - EA_H = 4.478-0.754 = 3.724 \) eV \( (D(H_2) \) - dissociation energy of \( H_2 \); \( EA_H \) - electron affinity of \( H \)). If the target molecule is in an excited vibrational state it will need less energy for dissociation and therefore the DEA threshold will be lower by excitation energy. This, together with the fact that the CS for DEA strongly increases with target excitation, is the basis of the present method. Above characteristics of DEA depend only on electronic states involved in the process so that same spectroscopic method is applicable to HD and D\(_2\) and other hydrogen isotopomers.

In order to enable efficient vibrational spectroscopy new experimental set-up was constructed. Magnetic field is used in this set-up for electron beam collimation and for selective detection of desired negative ions. The first of vibrational spectrometer that was employing same measurement principle [13] was using electrostatic electron energy filter and quadrupol mass filter for ion separation.

Basic arguments for the choice of instrument that is using magnetic field are related to better control of electron beam at very low energy, higher current of low energy electron beam and simpler and more compact design. Original ion extraction optics is employed in the present set-up that is described in detail elsewhere [14]. Electrode system of the present set-up
is schematically shown in two cuts in figure 1. Modular approach is followed so that both, electron beam and ion detection are mounted on the sides of the central mounting block, an 8 cm cube. Sample gas is introduced at the top of this mounting block.

Figure 1: Schematic view of electrode arrangement of vibrational spectrometer: a) horizontal and b) vertical cut. Guiding magnetic field is produced by external pair of Helmholtz coils.

Electron beam is produced by a simple low resolution electron gun or by higher resolution trochoidal electron monochromator (not shown in figure). Special ion extraction optics use field penetration technique for highly efficient low energy ion collection. Ions are detected by an off-axis channel electron multiplier. In designing the new system we were using CPO3D software for electron and ion trajectory simulations (http://www.electronoptics.com).

In general appearance present spectrometer looks similar to specific mass spectrometer. It operates so that extraction optics is tuned to detect H- or D- ions and then electron beam energy is scanned. For obtaining vibrational spectrum one scans e-beam in the range between 0 and 5 eV (4eV process). Electron beam energy is scanned in the broader range between 0 and 20 eV if one wants to observe simultaneously with 4 eV process also other processes (14eV in hydrogen, 6.2eV in background water and possibly ions from some other impurities). Experimental spectrum is therefore ion yield as a function of electron energy.

2.2 Hydrogen depth profiling by ERDA

In order to have deeper insight into studied surface processes we also perform in-situ hydrogen depth profiling for particular experimental conditions. This is done by Elastic Recoil Detection Analysis (ERDA) at ERDA/RBS measurement station at 2MV tandem accelerator at Jozef Stefan Institute. Hydrogen (H and D) concentration at the surface and bellow the surface (in the bulk) can be determined from energy spectra of recoiled particles.
We use 4.2 MeV probing beam of $^7$Li$^{2+}$ ions [11]. Studies of hydrogen interaction with tungsten were performed with specially designed hydrogen exposure cell [15] and hydrogen permeation through Pd membrane was also studied by ERDA [16].

2.3 Source of hydrogen molecules created by recombination at the surface

Different experimental arrangements can be considered in order to perform studies with vibrationally excited hydrogen molecules. At the present we started two series of experiments regarding vibrational excitation of molecules created by recombination on the surface. In one experiment we are studying vibrational excitation of molecules created at the surface exposed to a partially dissociated neutral hydrogen atmosphere. In another experiments molecules that are formed after hydrogen atom permeation through the thin metal membrane are studied. These two experimental arrangements are described and some results presented here.

2.3.1 Source of vibrationally excited hydrogen molecules

Simple gas cell that contains resistively heated tungsten filament is used for producing vibrationally excited hydrogen molecules. It operates on the same principle as similar cell used for extensive studies in the past [17]. The cell that is presently used for the studies is shown in figures 2 and 3. It is a compact pancake structure made of copper that is mounted on the top of 8 cm mounting block of vibrational spectrometer (also shown). Top section of the cell is cooled by water flow from a closed refrigeration system. Pressure in the cell is measured by capacitance manometer.

Hydrogen gas is introduced into the cell where it is dissociated by a hot tungsten filament, 0.2 mm in diameter. Rate of dissociation is controlled by filament temperature i.e. by the heating current through the filament. Excited molecules are produced by recombination of atoms on the cold wall and after number of volume and surface collisions they leave the cell through the 6 mm in diameter exit orifice. Sample plate (20 mm dia.) of studied material is mounted on the cold finger just in front of the exit orifice of the cell. Distance between sample plate and the plane of orifice is 4 mm. Hydrogen gas containing hot molecules flows out of the source and it is intercepted by probing electron beam of vibrational spectrometer. Negative ions created by DEA are collected by an extraction system and then detected by a channel electron multiplier.

![Figure 2: Schematic view of the source of vibrationally excited molecules used in the present study.](image)
Geometry of the source ensures that molecules that are created at the sample plate have as straight as possible path to the exit of the cell. However, more detailed modelling is needed in order to quantitatively characterise the processes that take part in the cell – recombination and vibrational relaxation. Development of the appropriate code is in progress.

2.3.2 Permeation source

For a particular study of recombination of atoms that arrive on the surface after permeating through the bulk we are using specially designed permeation source. Metal membrane is soldered on a small stainless-steel cylinder with diameter of 10mm. This membrane holder is welded on a smaller tube and attached by standard fitting to the gas cylinder. This membrane assembly was mounted at the top of vibrational spectrometer facing electron probing beam. Inner side of the membrane is exposed to a high pressure of hydrogen (typically 1bar), while the outer side of the membrane faces background vacuum. The membrane’s temperature is controlled by a heater wrapped around the 10mm tube and monitored by a thermocouple inserted in a small hole in the 10mm holder. First measurements were performed with 100μm thick palladium membrane.

3 RESULTS

Measurements with the source of vibrationally excited hydrogen were performed with Ta (0.5mm thick) and Cu (1mm thick) disks mounted in front of the exit orifice. Hydrogen flow through the cell is such that pressure in the cell is varied between 0 and 2 μbar. Dissociation filament temperature is varied in the range between 1300 K ($I_{\text{dis}}=2.8$A) and 1700 K ($I_{\text{dis}}=4.4$A).

One example of vibrational distribution of H$_2$ molecules with Ta disk mounted in the cell is shown in figure 4. In figure 4a the experimental spectra of H$^+$ yield vs. electron energy for different dissociation filament temperature are shown. For the cold gas (purple line and shaded below it), i.e. zero or low heating current $I_{\text{dis}}$, only one peak at around 4eV is present that is due to the DEA to vibrational ground state molecules. When dissociation filament is heated, created atoms recombine on the cold surface thus producing excited molecules. Their presence is manifested by appearance of H$^+$ ions at lower energy - threshold for DEA is lower for excited state than for the ground state by corresponding excitation energy. For the
practical reasons the electron energy scale is set so that \( v=0 \) peak is positioned at the corresponding DEA threshold energy, 3.72 eV although the real threshold is on the mid rise of the peak.

![Normalized H\(_2^+\) yield as a function of incident electron energy obtained when H\(_2\) is introduced into the source of vibrationally excited molecules (a) and corresponding relative state distributions (b).](image)

By using appropriate fitting procedure that makes use of the most recent theoretical cross sections [18] we determine relative populations of different vibrational states – shown in figure 4b. Vibrational states are indicated on both figures. Indicated populations of the highest vibrational states, \( v=8 \) and 9 in the case of H\(_2\) are not reliable due to the problems with electron beam at low electron energy. Vibrational populations that correspond to the Boltzmann distribution for the indicated vibrational temperatures are also shown in figure 4b. One can see that for lower filament temperature the vibrational distribution exhibits two vibrational temperatures, around 3200K for lower and 5000K for higher states. At higher filament temperatures, i.e. higher rate of dissociation in the cell the distribution is well characterised by single vibrational temperature, around 3500K that does not depend on \( I_{\text{dis}} \).

Negative ion yield spectra for the case of D\(_2\) are shown also for three temperatures in figure 5a and corresponding vibrational distributions in figure 5b. One of important characteristics of 4eV DEA in hydrogen is its spectacular isotope effect. Cross section for D\(^-\)/D\(_2\) production is about 300 times smaller then for H\(^-\)/H\(_2\) for the molecules in ground vibrational state. However, for vibrationally excited states these cross sections become very high, in the range of \( 10^{-15} \) cm\(^2\), for all hydrogen isotopomers. This fact is illustrated when comparing spectra for H\(_2\) and D\(_2\) in figures 4 and 5, respectively. Contribution of D\(_2\) in \( v=0, 1 \) and 2 states to D\(^-\) production is negligible while for the higher states it is comparable to the H\(^-\) production from H\(_2\). Another, more “technical” difference between DEA in H\(_2\) and D\(_2\) is that, due to smaller vibrational spacing in D\(_2\), vibrational thresholds are less separated in this isotopomer then in lighter H\(_2\). Vibrational temperatures between 3400K and 4600K are deduced from the population analysis (figure 5b) with similar double distribution for low atomic fluxes as in H\(_2\).

Study of isotope effects is of high importance for fusion edge plasma as D\(_2\) and T\(_2\) are the fuel there. Studies with H and D allow deeper insight into the processes and therefore also more reliable estimates for T as well. In our future studies it will be of special interest to study...
also HD production when both \( \text{H}_2 \) and \( \text{D}_2 \) are present in the source of vibrationally excited hydrogen. For this we have still to improve performances of our vibrational spectrometer in the sense of better energy resolution and mass separation.

![Figure 5](image)

**Figure 5:** \( \text{D}^- \) yield as a function of incident electron energy obtained when \( \text{D}_2 \) is introduced into the source of vibrationally excited molecules (a) and corresponding relative state distributions (b).

Our source of vibrationally excited hydrogen allows also qualitative studies of reactions among excited neutrals of different molecules of interest for fusion plasma. By introducing impurities that are present there such as water or different hydrocarbons alone or in mixture with hydrogen one can observe potential alternative reaction channels that might lead to vibrationally excited hydrogen production.

In order to extract quantitative information on state selective recombination rates and vibrational relaxation rates from experimental vibrational distributions we need to perform detailed modelling of the source of vibrationally excited molecules. This work is in progress and initial results are expected in coming months.

Result of our first study of recombination after H permeation through palladium membrane is show in figure 6. Membrane temperature and background pressure are indicated in figure. Part of the pressure rise is due to the enhance outgassing when permeation assembly is heated. For this study permeation assembly was mounted at the top of vibrational spectrometer so that molecules released from the vacuum side of the membrane are directly intercepted by the probing electron beam. We have performed also a detailed analysis of permeation through the same membrane by ERDA [16]. Initial result of vibrational spectroscopy of molecules produced by recombination on Pd (figure 6) shows that molecules are created in ground vibrational states. However, the noise below \( v=0 \) peak does indicate that some of this signal might arise from less abundant excited states. Further studies of hydrogen recombination after permeation are in progress in order to give deeper insight into the recombination process. Studies will be repeated with higher statistics but also with deuterium that would give increased relative sensitivity to high-\( v \) states. Permeation through some other metal membranes will be performed as well.
Figure 6: $^1$H/$^2$H yield as a function of electron energy. $^2$H molecules are introduced into interaction region of vibrational spectrometer by permeation through 100 $\mu$m Pd membrane.

Further experimental studies are planned with new vibrational spectrometer described here but also with the old one [13] that we have available in our laboratory. This include experiments with H (D)-atomic source, study of thermal desorption, vibrational spectroscopy of molecules from discharges and similar.

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