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Reemission of neutral hydrogen molecules from tungsten

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ABSTRACT

Vibrational distribution of H_2 and D_2 molecules emitted from tungsten surface exposed to the continuous flow of partially dissociated neutral hydrogen gas is studied. A special vibrational spectrometer is used for this study. Vibrational distributions can be well described by vibrational temperatures being $T_V = 3700 \pm 100$ K for H_2 and $T_V = 3400 \pm 100$ K for D_2. To gain more detailed information on the state of the tungsten surface we employed ion beam analytical method ERDA for in situ determination of H/D concentration. Both experiments indicate high importance of impurity layer (presumably oxide) on the observed phenomena.

1. Introduction

Hydrogen recycling is an important process on the wall of a fusion reactor. Hydrogen ions that hit the wall surface after being neutralized may return into the plasma as neutral atoms or if they recombine with other atoms as neutral hydrogen molecules. Neutrals are predominantly reemitted as molecules at low surface temperatures while atom reemission dominates at higher temperatures [1]. Molecules produced at the surface can be vibrationally excited. These molecules are important for energy exchange between the edge plasma and the reactor wall and together with other charged and neutral particles they determine the characteristics of the edge plasma and therefore plasma–wall interaction. Excited neutral hydrogen molecules are produced not only on the surfaces in direct contact with the plasma but also at more remote surfaces such as are the gaps of castellated structures and the wall of the vacuum vessel. Rate of production and relaxation of the excited molecules as well as cross sections for different collision processes where they participate need to be known in order to enable detailed modelling of the edge plasma (e.g. [2]). Reaction rate constants often strongly depend on the internal excitation of participating particles so that this excitation can even alter the series of dominant reactions occurring close to the wall.

There is quite a lot of experimental data on hydrogen retention and release for W. On the other hand there is to our knowledge almost no experimental data on vibrational distribution of hydrogen molecules emitted from the tungsten surface and very little data on interaction of hydrogen atoms and molecules, with low kinetic energies (few meV), with the tungsten surface. In order to acquire new quantitative data on processes with vibrationally excited hydrogen molecules we are studying interaction of hydrogen atoms and molecules with high-Z materials and some results obtained with tungsten are presented in this paper. Terms 'hydrogen molecule' and 'hydrogen atom' are used in the text as a general designation for all hydrogen isotopologues or isotopes and chemical symbols H and D are used when isotopic composition of a particle is relevant.

2. Experiment

Experiments were performed using two diagnostic techniques on separate experimental set-ups [3].

For vibrational spectroscopy of H_2 and D_2 we employ a method based on properties of the lowest energy dissociative electron attachment (DEA) in hydrogen, $e + H_2 \rightarrow H^- + H$ or $e + D_2 \rightarrow D^- + D$. Vibrational temperature of target gas is determined by deconvolution of experimental negative ion (H^- or D^-) yield spectra. These spectra represent dependence of negative ion yield on the energy of electron beam in the 0–5 eV range. A new set-up (DTVE-B) employing this method of vibrational spectroscopy was developed in order to facilitate studies of processes involving vibrationally excited hydrogen molecules [3,4]. A special source of vibrationally excited hydrogen molecules (TS) was used for the present studies and it is shown in Fig. 1(a). Hydrogen gas is introduced in the cell where it becomes partially dissociated by a hot tungsten filament. Atoms that are created on the filament can eventually recombine on the cooled wall surface and vibrationally excited molecules are created depending on the conditions in the cell and wall material [5]. Gas containing vibrationally cold ($v = 0$) and hot ($v > 0$) molecules as well as atoms which did not recombine flows out of the cell through the exit orifice and is being intercepted by the electron beam of DTVE-B (Fig. 1(b)). A disk of the studied material (25 mm dia.) is placed close (5 mm) and parallel to the exit orifice

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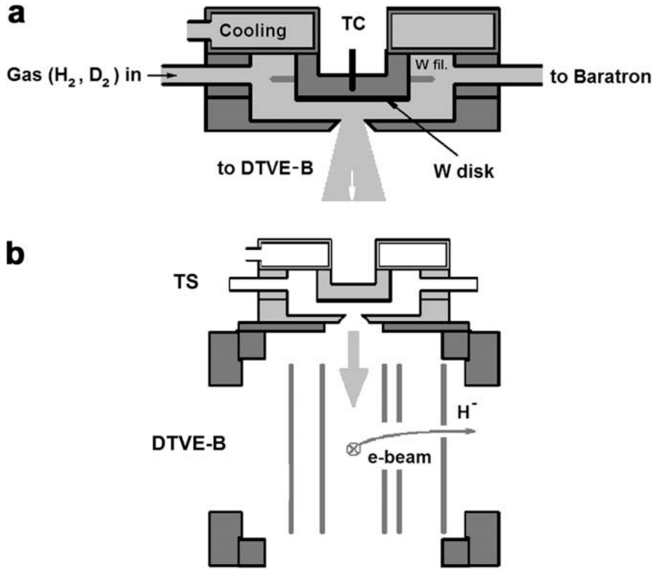

Fig. 1. Source of vibrationally hot hydrogen molecules – TS (a) and its position at the assembly of vibrational spectrometer DTVE-B (b).

(6 mm dia.) so that recombination at the sample disk determines to a large extent the vibrational composition of the effusing gas. Pressure in the cell is measured by a capacitive manometer and is typically in the 10^{-3} mbar range. Temperature of the sample is measured by thermocouple (TC) and can be varied by adjusting cooling intensity.

The ion beam analytical method ERDA (elastic recoil detection analysis) is used for determination of H and D concentration on the sample surface under similar conditions as in TS but on another experimental station. Special gas-cell, HEC (hydrogen exposure cell), was constructed for in situ ERDA studies of hydrogen interaction with material [6]. It operates on the same principle as TS (hot dissociation filament and cooled wall) but gas in HEC is more stagnant as it only leaks out through the narrow gaps of intentionally not vacuum-tight assembly. A 4.2 MeV $^7Li^{2+}$ ion beam was used for H and D depth profiling by ERDA. Angle between the incident ion beam and the sample surface is 15° and recoiled H and D are detected in forward direction also at an angle of 15° with respect to the sample surface. For determination of absolute concentrations of H and D from ERDA spectra we use SIMNRA program (http://www.rzg.mpg.de/~mam/). Accurate cross sections for elastic ^{7}Li–H scattering are used for determination of the H concentration. Such cross sections are not available for the ^{7}Li–D so that we used classical Rutherford elastic recoil cross section [7] for determination of D concentration.

Samples for both experiments were made of 0.3 mm thick rolled 99.95% pure tungsten foil purchased from Goodfellow. Tungsten was treated by standard cleaning and then polishing by alumina powder wetted in tetrachloromethane (organic solvent not containing hydrogen). Samples were not heated to high temperature and annealed before experiments.

3. Results

3.1. Vibrational distribution of H_2 and D_2 produced by recombination on W

An H^- yield from DEA obtained when H_2 was introduced in TS, with the sample disk made of tungsten, is shown in Fig. 2(a) (dots). Positions of maximal contribution to H^- production from particular vibrational state are marked by vertical lines and the corresponding vibrational level is indicated on the top. Dissociation filament is 12 cm long, 0.3 mm dia. W wire (filament f1) and its temperature was about 2000 K. The shape of the vibrational distribution of H_2 does not depend on the filament temperature and consequently on atom flux density but dominantly on the recombining surface. Also shown in Fig. 2(a) (dashed line) is H^- yield obtained with the filament turned off, i.e. for cold (only $v = 0$) hydrogen gas. Only single peak is observed here corresponding to DEA to the cold molecule having threshold at 3.73 eV. Spectrum from Fig. 2(a) was taken under standard conditions for TS operation in the present series of measurements. Sample temperature was between 13 °C and 15 °C. Gas pressure in the cell was 9×10^{-4} mbar corresponding to the impinging rate (H_2 equivalent) of 9.9×10^{17} cm^{-2} s^{-1}. Total H_2 flow rate through the source is 1.8×10^{17} molecule/s (0.4 sccm). We used a method developed at IPP, Garching, [8] for determining atom impinging rate in order to better understand the exposure conditions. This method is based on measurement of reduction of the thickness of amorphous hydrogenated carbon film. This reduction is a consequence of chemical erosion by hydrogen atoms and it is proportional to the total atom fluence. Such hydrogenated carbon film was mounted in TS and exposed to similar hydrogen atmosphere as the W sample. The impinging rate of H^- atoms in the region facing exit aperture of TS was determined to be 1.7×10^{15} atoms/(cm^2 s). A spectrum of D^- yield obtained under similar TS conditions but with D_2 introduced in the cell is shown in Fig. 2(b). Vibrational structure here is less pronounced due to smaller vibrational spacing in deuterium. Very small (300 times smaller than in H_2) DEA cross section for D_2 in $v = 0$ state is the reason that there is hardly detectable production of D^- in cold gas. However, the cross section in D_2 increases much faster with the vibrational excitation than in H_2 so that cross sections for both cases have similar values once the energy of internal excitation is above 2 eV [9]. This value is in the 10^{-16}–10^{-15} cm^2 range for all hydrogen isotopologues.

Experimental H^- or D^- yield for hot molecules when deconvoluted gives relative vibrational population for individual vibrational state. Calculated spectra obtained from deconvolution procedure for the two cases are shown in Fig. 2 together with the experimental ones and the resulting relative populations are shown in Fig. 3 and are designated by ‘f1’. Relative populations of vibrational states of H_2 and D_2 obtained from the measurements performed with dissociation filament made of 0.2 mm dia. tungsten thoriated wire are also shown in Fig. 3 and designated by ‘f2’. From these and other measurements of vibrational population of molecules created by recombination on W one obtains consistently vibrational distributions which have rather Boltzmannian distribution corresponding to vibrational temperature $T_V = 3700 \pm 100$ K for H_2 and $T_V = 3400 \pm 100$ K for D_2. It is necessary to state here that vibrational spectra are often quite different even when recorded under apparently identical conditions and also they often vary with time (e.g. relative intensity of the vibrationally excited molecules decreases with time). This is presumably due to the presence of an oxide layer on the surface of the sample. This layer certainly gets modified under hydrogen atom impact on the surface and therefore its properties related to atom recombination can vary. However, even these differences of ion yield spectra are observed they are such to keep the vibrational temperature within the stated interval. Vibrational temperature determined in the present experiment for H_2 is lower than in an earlier study of similar type but with in situ evaporated tungsten film [5]. This difference might be a consequence of the oxide layer presumably present on the W sample disk used in the present experiments. Energy resolution of our method is not sufficient to enable determination of the population of individual rotational states but spectrum deconvolution procedure provides an estimate of the rotational temperature. Namely, in this procedure all rotational

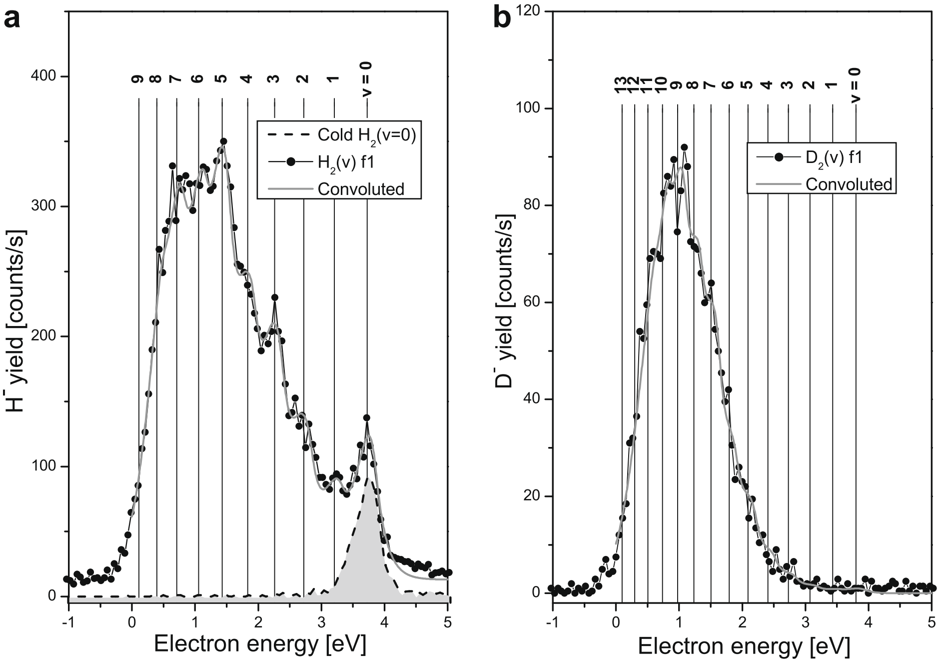

Fig. 2. H^- (a) and D^- (b) ion yield versus electron beam energy for vibrationally excited H_2 and D_2 gas respectively. Dissociation filament is 0.3 mm dia. tungsten wire (f1).

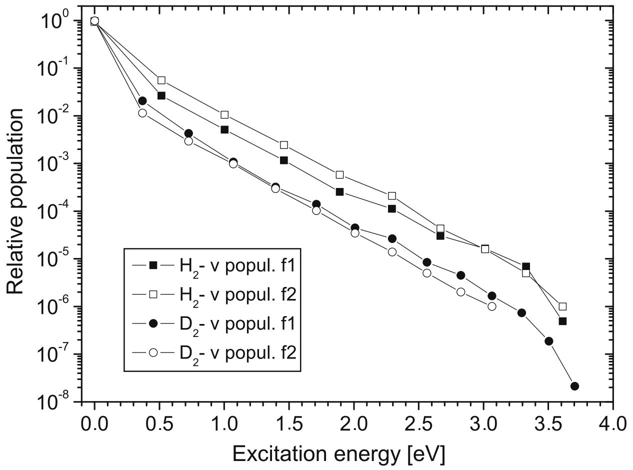

Fig. 3. Relative populations of vibrational states of H_2 and D_2 molecules obtained by deconvolution of ion yield spectra. Distributions designated by 'f1' are obtained for spectra from Fig. 2 while distributions designated by 'f2' are obtained from measurements when a 0.2 mm dia. thoriated tungsten wire was used as the dissociation filament.

and vibrational states are taken into account when calculating spectrum to be compared to the experimental one. A rotational temperature is a parameter of convolution fitting procedure and it influences the width of individual vibrational peak in the spectrum. Accordingly an increase of the rotational temperature leads to broadening of the individual vibrational peaks. For the case of H_2/W and D_2/W from Fig. 2 these temperatures are around T_R = 700 K and 300 K, respectively.

Our hydrogen vibrational spectroscopic studies have been regularly revealing a presence of certain detection noise in ion yield signal that is independent of electron beam energy. This noise appears at higher tungsten filament temperature only if hydrogen is present in the cell. It is visible in Fig. 2(a) as a small upward shift of the whole ion yield curve. This noise is presumably due to the metastable neutral particles produced by hydrogen interaction with hot tungsten. More experiments are needed to definitively identify these particles and also a mechanism for their production.

3.2. H and D concentration on W

H and D concentration on tungsten sample mounted in HEC (same material as used in TS) was studied by ERDA technique. Initial experimental ERDA spectra exhibited pronounced surface peak of H and only a weak H signal from bulk. This is due to the low hydrogen solubility in tungsten. As a consequence of dominant surface concentrations, the H and D signals appear as two well-separated peaks. This enabled us to study variation of H and D surface concentration under very similar conditions to those that we had in the study of vibrational excitation from TS. One example of time variation of H (squares) and D (dots) surface concentration measured on the W sample in HEC is shown in Fig. 4. Each pair of points corresponds to one ERDA spectrum and presents absolute surface concentrations of H and D. Typical signal accumulation time for one spectrum was about 10 min. Gas pressure in the cell, sample temperature and heating current (I_{dis}) through the dissociation filament (0.3 mm dia. tungsten wire) are also shown in Fig. 4. Impinging rate of molecules during isotope exchange was 1×10^{18} D_2 mol/cm^2 s at pressure 1.33×10^{-3} mbar. Dissociation rate of the deuterium gas at I_{dis} = 3 A, corresponding to filament temperature 1600 K, is about 1% or even less. During initial sample exposure to molecular deuterium (from 60 min to 220 min) only weak build-up of D surface concentration is observed. Very fast isotope exchange occurs once the dissociation filament is turned on and D atoms start to impinge the surface. After initial fast isotope exchange D concentration stabilises but H intensity continuously decreases with a slower rate. This is presumably due to the reduction of oxide layer at the sample surface. During surface exposure to deuterium molecules and atoms sample temperature was varied in order to see whether there would be any noticeable variation in surface concentration, i.e. adsorption and recombination. Precise balance of total, H plus D concentration on the surface can not be evaluated as absolute D concentration is directly related to the incertitude of employed Rutherford cross section for elastic ^{7}Li–D scattering. Observed slow variation of surface H and D con-

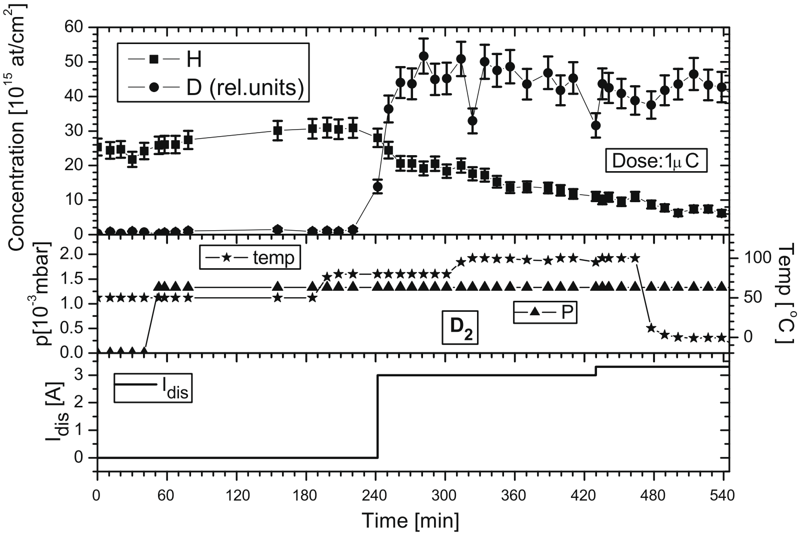

Fig. 4. Time variation of surface concentration of H and D during continuous exposure to deuterium under different conditions (top). Pressure in HEC, sample temperature (middle) and heating current through the dissociation filament (bottom) characterise the exposure conditions. Surface concentrations were determined from ERDA spectra with 4.2 MeV $^7Li^{2+}$ ion beam.

centrations explains also the observed variations of measured vibrational spectra in experiments with DTVE-B. Rather high surface concentration of H and D are detected as compared to the pure tungsten surface (monolayer for 001 surface corresponds to 1×10^{15} atoms/cm^{-2}). Part of this higher concentration can be attributed to the polycrystalline character of the used sample and also to the surface roughness but still, the measured initial value of H concentration indicates presence of some impurity (presumably oxide) layer on our sample. A thin oxide layer was observed by later XPS analysis of the sample.

4. Discussion

Vibrational temperature of H_2 and D_2 molecules reemitted from tungsten surface which is continuously exposed to the flow of atoms and molecules is shown to be high. A free hydrogen atom when recombining with chemically adsorbed atom brings 2.24 eV of potential energy (one half of the dissociation energy of hydrogen molecule) to the desorbed molecule. This kind of recombination is the so-called Eley-Rideal mechanism. In the case of tungsten the hydrogen adsorption energy E_{ch} is equal to 0.66 eV [10] and molecule desorbes with a maximum available energy of 2.24 eV – E_{ch} being equal to 1.58 eV. This allows the population of vibrational levels up to $v = 3$. Therefore, the classical Eley–Rideal mechanism can not explain the population of higher states. On the other hand it can be attributed to the Eley–Rideal like recombination of free atoms with relatively loosely bound, so-called 'hot' hydrogen atoms [11] at the surface [12,13] or to the recombination of two hot atoms. Properties of a layer of these hot hydrogen atoms and rate of energy transfer from these hot atoms to the metal surface are strongly dependent on the properties of the surface and also on the surface temperature. Measurements with ERDA method under similar conditions bring additional insight on the surface conditions that determine atom recombination and molecule reemission.

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