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Reflection and adsorption of deuterium atoms and molecules on graphite

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Abstract

For determining the reflection and adsorption coefficient of deuterium atoms and molecules on graphite, a mixed beam of deuterium atoms and molecules with temperatures above 2000 K was directed to a graphite surface and the amount of released D^0 and D_2 was determined by line-of-sight mass spectroscopy. The velocity distributions measured by the time-of-flight (TOF) signal were used to distinguish the directly reflected particles from desorbed particles. The main results are: the released deuterium atoms showed the energy distribution of the incident beams. The reflection coefficient for deuterium atoms (above 2000 K) on graphite was about 0.7 and decreased with longer exposure time of graphite by deuterium atoms. Part of the released deuterium molecules showed the distribution of the incident beam: they were reflected without losing energy. The reflection coefficient for deuterium molecules (above 2000 K) on graphite was between 0.7 and 0.8. Most of the adsorbed deuterium was released as molecules with Maxwell–Boltzmann velocity distribution of the target temperature. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The hydrogen recycling on plasma-facing materials largely affects the fueling efficiency of fusion plasmas. Recycling includes both the re-emission of implanted or adsorbed hydrogen and the reflection processes. We will consider here only the hydrogen behavior on carbon materials. It is important for plasma-edge properties whether the hydrogen recycles forming a molecule or an atom. It was shown earlier that for temperatures above 1000 K hydrogen ions from beams or from TEXTOR plasmas implanted into graphite were mainly released as atoms [1,2]. It is not clear whether the adsorbed hydrogen atoms will be desorbed as atoms or as molecules after the recombination at temperatures above 1000 K.

For energetic ions, the reflection process is an ion–atom scattering between the incident ion and the target atoms which leads to charge transfer, energy loss and momentum transfer. As a result of the scattering on the graphite surface the energy distribution of the reflected hydrogens become broad from zero up to a value of 0.8 of the incident energy, most of the reflected hydrogens become neutral and for normal incidence the angular distribution of reflected hydrogens is close to a cosine distribution. For larger angle of incidence, the distribution becomes peaked around the direction of specular reflection [3,4] and the reflection coefficient increases with the angle of incidence. Experimental reflection data of hydrogen and deuterium on graphite exist for energies down to 30 eV [5,6] and they agree with TRIM (Monte Carlo Simulation) calculations [7]. However, very little is known about the reflection and adsorption of hydrogen atoms and molecules at lower energies. In model calculations [7], the reflection coefficients below 1 eV decrease to 0 due to the influence of the surface binding energy. However, if the incident atom finds no possible

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way to dissipate the kinetic energy the reflection coefficient could be close to one. In this low energy range, the most effective mechanism in energy transfer is the excitation of phonons in the adsorbing surface [8]. In the study of model calculation of low temperature plasmas the reflection coefficient of hydrogen atoms is used as a fitting parameter, and mostly a value close to one is employed [9,10].

The hydrogen-covered graphite surface or the hydrogen bonded to the carbon atoms in the graphite surface could also influence the reflection coefficient. In TRIM calculations for energetic hydrogen ions the reflection coefficient is smaller for hydrogen containing amorphous layers (a-C:H films) [5].

The amount at which the reflection of hydrogen occupies the entire recycling is important in determining the fueling efficiency of the fusion plasma since the energy of the reflected hydrogen is higher than that of the thermally re-emitted one and thus the penetration of the reflected hydrogen back into the plasma before it gets ionized is much deeper. For modeling the divertor plasma it is essential to know the reflection coefficient of hydrogen isotopes at low energies.

2. Experimental and data evaluation

To determine the reflection and adsorption coefficient of atomic and molecular hydrogen (deuterium) on graphite, a mixed beam of atomic and molecular hydrogen (deuterium) with temperatures between 2000 and 2680 K is directed under an angle of 45° to a graphite surface and the amount of released H⁰ (D⁰) and H₂ (D₂) is determined by line-of-sight mass spectroscopy. The velocity distributions measured by the time-of-flight (TOF) signals are used to distinguish the directly reflected particles having the distribution of the incident beam from the desorbed particles that show the distribution corresponding to the equilibrium with the target temperature.

Details of the experimental set-up are described in previous papers [11,12]. Briefly, pyrolytic graphite (Union Carbide, HPG) samples were bombarded by a mixed beam of 4×10^{19} H⁰/m² s and 8×10^{19} H₂/m² s (or 1×10^{20} D⁰/m² s and 7×10^{19} D₂/m² s) in the case of 2440 K source (tungsten tube) temperature. From a vapor pressure calculation, the tungsten impurity in the beam should be of the order of 2×10^{12} W/m² s. The emitted particles were periodically chopped on a motor driven disk with a trapezoidal transmission pulse (HWFMT = 13 μs, repetition time 700 μs) and were directly detected after a flight path of $s = 15$ cm by a differentially pumped line-of-sight quadrupole mass spectrometer (QMS) aligned at 90° with respect to the incident beam direction. The signals were collected in a multichannel counting device (2 μs channel width) which

directly records the TOF spectra, including the TOF data and the TOF in the QMS of the ionized particles. The zero line of a TOF spectra was obtained by averaging the noise at large TOFs and using this value as the background signal. The sensitivity of the detection system has been calibrated by measurements of H₂ and D₂ fluxes from a heatable Knudsen cell in the target position. Using literature values for the ionization cross-section for H₂ and D₂ [13] the ratio of the transmission for mass 4 to mass 2 ($M4/M2$) was determined to 0.8. This ratio is in good agreement with 0.86, the value determined from the cracking of D₂. From the cracking of H₂ the transmission ratio of $M1/M2$ was determined to 0.34. For two reasons we will only report the result for the reflection coefficient of D and D₂. Firstly, the noise at $M2$ is much larger than the noise at $M4$ and as we will report in this paper the re-emission of the molecule shows a more complicated spectra and needs to be measured more precisely which is only possible for $M4$. Secondly, the determination of the transmission by the cracking alone seems to be too uncertain. The result of re-emission study with H atoms is used mainly to demonstrate the qualitative dependence under different conditions.

The signal distribution function is given by: $S(t) = \int_0^\infty w(t - L/v)\phi(v)\eta(v) dv$, where $\eta(v)$ is the ionization efficiency in the ionizer of the QMS (inversely proportional to the velocity $v \propto \sqrt{T/M}$), $w(t)$ is the window function of the selector, L the pass length of TOF and $\phi(v)$ the velocity distribution of the flux. The signal $S(t)$ can be numerically calculated for arbitrary $w(t)$, $\phi(v)$ and $\eta(v)$. In the case of relatively short transmission pulses, the maximum value of $S(t)$ is proportional to the absolute flux ϕ_0 for the same type of velocity distribution $\phi(v)$ [14].

The reflection coefficient is determined by the assumption that the retention of atomic and molecular hydrogen in graphite is negligibly small (in Ref. [15] the retention is estimated to 4% at the beginning of hydrogen atom exposure and decreasing with further fluence). The fluxes of D and D₂ are calculated by a simple theory from the temperature of the source and the flow rate through the aperture of the source [15]. The following relations are used: $\Phi_D^* = \Phi_D^0 R_D$, $\Phi_{D_2}^* = \Phi_{D_2}^0 R_{D_2}$ and $\Phi_{D_2}' = 0.5\Phi_D^0(1 - R_D) + \Phi_{D_2}^0(1 - R_{D_2})$ where Φ_D^0 and $\Phi_{D_2}^0$ are the incident atomic and molecular fluxes, Φ_D^* , $\Phi_{D_2}^*$ are the reflected atomic and molecular fluxes, Φ_{D_2}' is the desorbed molecular flux and R_D and R_{D_2} are the particle reflections coefficients for deuterium atoms and molecules, respectively.

3. Results

Fig. 1 shows a typical TOF spectrum of re-emitted D (upper curve) and D₂ for a mixed incident beam of D

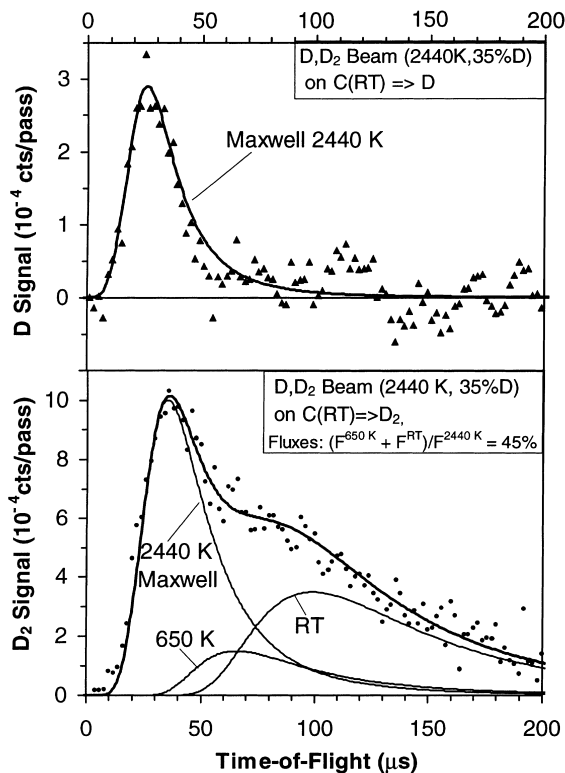


Fig. 1. Typical TOF spectrum of reflected and re-emitted D (top) and D₂ (bottom) during D/D₂ impact on graphite at RT under 45°. Thin solid lines are calculated Maxwell–Boltzmann distributions with given temperatures, thick one is the sum of all.

and D₂ on graphite. In this case the temperature of the beam is 2440 K. Generally in all observed results, the D (H) spectra consist of only one component with the incident beam temperature. The D₂ (H₂) spectra consist of two or three components. The largest one has the incident beam temperature and the slowest one shows the target temperature. In some distributions, as in Fig. 1(b), a third distribution has to be taken into account to fit the experimental result. For simplicity a Maxwellian has also been chosen, in this case one of 650 K. In this medium temperature range a distribution other than the Maxwellian would be possible. It is obvious that the beam temperature component stands for an elastic reflection without energy loss, and the target temperature component corresponds to the group formed by desorption of the adsorbed D or D₂. The medium energy distribution, described by a 650 K Maxwellian, could be from D₂ reflection with loss of energy or an overthermal desorption due to recombination which is similar to the effect observed in hydrogen desorption from tungsten [16].

The quantitative estimation of the reflection coefficient is more difficult. The incoming beam intensity

cannot be measured directly, but is determined by the calculation from the flow rate through the source and its temperature. Very important is the angular distribution. In our experimental device the angle between the beam and the axis of the line-of-sight detector is fixed to 90°. Only the target can be rotated, i.e. the incident angle can be changed. The result of such an experiment for H⁰ is shown in Fig. 2. The incident beam is so narrow that for all angles up to 60° with respect to the surface normal the total beam hits the target. This result suggests that H⁰ is reflected with a cosine angular distribution. The backward distribution is rather uncertain.

The determination of the reflection coefficient for D₂ is relatively straight forward using a beam of 2000 K which contains only 4% atoms. The result is $R_{D_2} = 0.8$. As soon as a beam with higher atom concentration is used a transient behavior is observed. At the beginning after a target baking at 1400 K the directly reflected peaks of D(H) and D₂(H₂) are more pronounced. After a longer irradiation these peaks are reduced without a detectable increase of the RT component as seen in Fig. 3, in which the shown spectra were taken at differ-

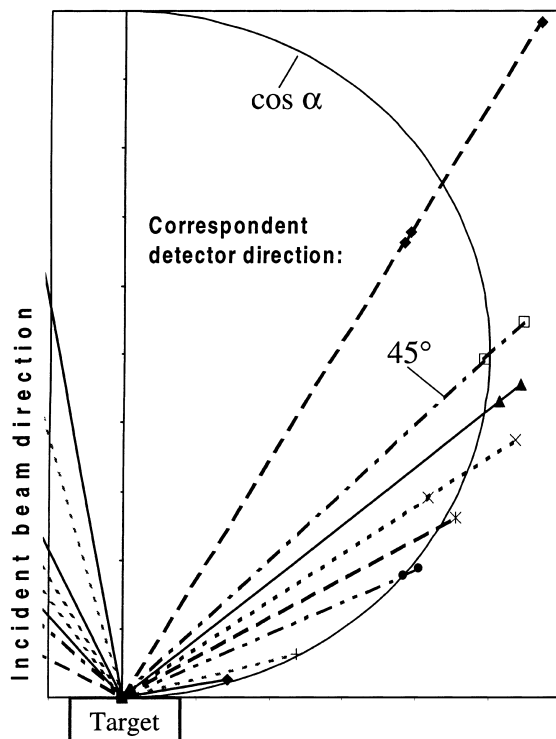


Fig. 2. Quasi-angular distribution of reflected H (2540 K) from graphite at RT in a polar diagram. The angle between beam and detector direction is fixed to 90°. Only the target can be rotated. Thus, for each incident direction only one detector direction is possible. The data were obtained in two experimental runs after a long-term irradiation.

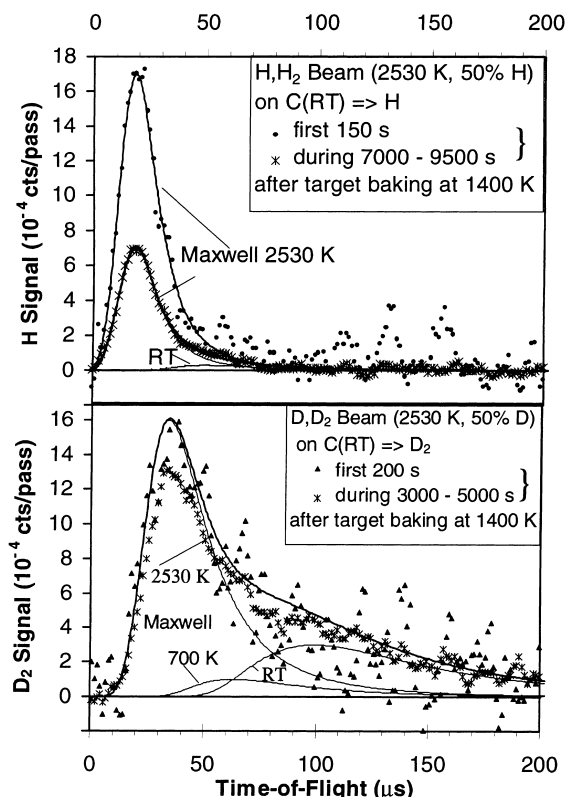


Fig. 3. TOF spectrum of H and D₂ re-emitted under 45° from graphite at RT for different exposure times after baking the target at 1400 K. Thin solid lines are calculated Maxwell-Boltzmann distributions of the given temperatures.

ent times of exposure in the same experimental run at an incident angle of 45°. The same data were also taken at an angle of 60° of the incident beam (the detector direction at 30°) with respect to the target normal. The obtained behavior of the spectra are very similar to the results at 45°. However, the reduction of the elastically reflected atomic hydrogen due to longer irradiation at this angle is only 30% whereas the reduction at 45° is 55% as seen in Fig. 3. A remark to the component in Fig. 3 (top) marked as RT. It is not clear whether or not a room temperature atomic hydrogen desorption occurs. The small deviation from the calculated 2530 K Maxwellian distribution for the long-term irradiation could also be caused by an incomplete correction of the cracking of the H₂ since the values for the H₂ component had to be taken from other experimental runs.

As already mentioned, if the decrease of the elastically reflected peaks with increasing exposure time is due to a decrease of the reflection in specular direction the increase in the RT component would be rather small. We have to conclude that this decrease of the direct reflection peak is mainly due to the modification of the surface by the hydrogen atom bombardment.

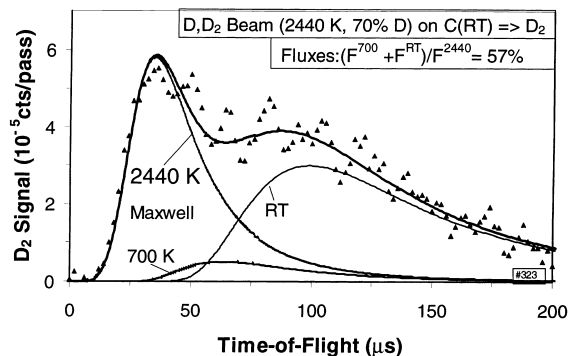


Fig. 4. TOF spectrum of emitted D₂ from graphite at RT at the same experimental conditions as Fig. 1 (subsequent exposure) except with 1/10 of flow rate through the beam source, i.e. a relative higher D content in the beam. Thin solid lines are calculated Maxwell-Boltzmann distributions of the given temperatures.

From a comparison of the result in Fig. 4 with Fig. 1(b) it is clear that incident atoms contribute to the RT component of the emitted D₂. The experimental run for Fig. 4 was done under the same experimental condition as in Fig. 1 except that 1/10 of the flow rate was used for the beam source, i.e., the ratio of D/D₂ in the beam was 2.4 instead of 0.55 for Fig. 1(b). The higher atom ratio in the beam effect an increase in the flux ratios of the two low *T* components (RT and 700 K) to the beam temperature component in the TOF spectra, namely from 0.45 in Fig. 1(b) to 0.57 in Fig. 4.

At higher temperature the peak of the largest TOF in the D₂ distribution fits with the target temperature as expected. Up to relatively high target temperature (900 K) no big change is observed. However, if we keep the target at 1300 K and above, only a small component with target temperature is left and parallel to this decrease the signal of the beam temperature component is increased. Also the signal of the emitted atoms is increased (Fig. 5). Since this temperature is above the thermal desorption temperature of implanted hydrogen or of an a-C:H film it is concluded that the hydrogen in the surface layer causes this change in the reflection behavior.

Using the relation described in Section 2 and trying to interpret the dependence on the beam temperature as a dependence on surface modification due to hydrogen atom irradiation the reflection coefficients under different conditions in Table 1 were obtained.

4. Discussion

An important observation is the reflection of over-thermal hydrogen/deuterium atoms and molecules without any energy loss, i.e., they are elastically reflected

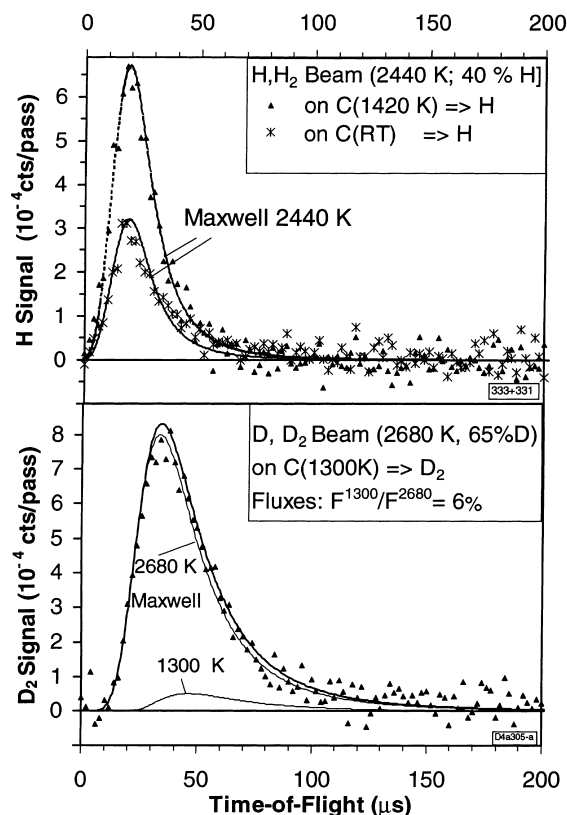


Fig. 5. TOF of re-emitted H (top) and D_2 (bottom) from a graphite target at 1420 K and 1300 K, respectively. Thin solid lines are calculated Maxwell–Boltzmann distributions of the given temperatures.

with the velocity distribution of the incident beam. This result can be associated with the mechanism that a particle will be reflected if no possibility exists to dissipate its energy [8]. Since for the elastically reflected atoms and molecules a cosine distribution is observed, we have to state that only momentum and not the energy of these particles is transferred to the target. The other point of view is also relevant: the reflection of low energy hydrogen on graphite is not only governed by a kinetic mechanism as in the high energy range, but the surface

Table 1

Reflection coefficients for D and D_2 (above 2000 K) on graphite at an incident angle of 45° . The error is estimated to be smaller as ± 0.2 .

	Low modified C	D rich C surface	C above 1400 K
R_D	0.75	0.65	0.9
R_{D_2}	0.80	0.70	0.9

chemistry plays an important role as it appears in the dependence on the modification of the surface by atomic hydrogen. The elastic reflection on modified surfaces after long hydrogen atom exposure is reduced for both atoms and molecules, which has been clearly observed in the long-term reflection experiment after baking the target to 1400 K (Fig. 3). This observation has a direct relevance for modeling the recycling of low energetic hydrogen on graphite since the surface of plasma-facing graphite components is mostly a hydrogen saturated layer or even an a-C:H film.

The behavior at high temperature is also remarkable. An earlier experiment [1] showed that in the case of hydrogen ion implantation or energetic plasma impact the re-emission of atoms from a high temperature surface seems to occur with target temperature velocity distribution. Such a behavior is not observed for hydrogen atoms on graphite. From the results in Fig. 5 it is seen that almost all atoms and the molecules are reflected with the energy distribution of the incident beam. This may be interpreted that during the short residence time an adsorption or energy exchange does not occur.

As already mentioned the quantitative estimation of the reflection coefficient is a rather difficult task. The incoming beam intensity cannot be measured directly and the quasi-angular distribution has only been determined for the low surface modification case. In the estimation of R_D and R_{D_2} the direct reflection component in specular directions assumed to occupy 20% of the signal of the beam temperature distribution and only 80% of the signal has been assumed to have a cosine distribution. Both of these are the most uncertain assumptions. Furthermore, the distribution at around 700 K is interpreted as an overthermal desorption after recombination of adsorbed atoms and also included in the calculation. Using these assumptions almost all measured distributions could be fitted within an error of ± 0.15 for R_D and R_{D_2} .

The trend for the lower reflection coefficient of the modified surface suggests that the reflection coefficient may be even smaller for an a-C:H film. This observation is satisfactory otherwise it would give rise to problems to explain the high reaction rate of hydrogen atoms with a-C:H films [12].

5. Summary and conclusion

The main results of the reflection and adsorption of hydrogen/deuterium atoms and molecules (≈ 2500 K) on graphite are:

- The released hydrogen/deuterium atoms showed the energy distribution of the incident beams with a cosine angular distribution, i.e. they are elastically reflected. The reflection coefficient for deuterium atoms (≈ 2500 K) on room temperature graphite is

about 0.7 and decreased with longer exposure time of graphite by deuterium atoms.

- Part of the released hydrogen/deuterium molecules showed the velocity distribution of the incident beam: They are elastically reflected. The reflection coefficient for deuterium molecules (≈ 2500 K) on graphite is between 0.7 and 0.8.
- Most of the adsorbed deuterium is released as molecules with Maxwell–Boltzmann velocity distribution of the target temperature.
- Within the experimental errors the reflection coefficients for hydrogen atoms and molecules are the same as those for deuterium.

The obtained reflection coefficients follow the trend which has been calculated and observed for hydrogen/deuterium ions above 30 eV, namely a reducing one for hydrogen-rich surfaces and an increasing trend with decreasing energy [5,6]. From our result it can be concluded that the influence of surface binding energy on the reflection has been overestimated in the model calculation [7] or in other words the problem of the energy dissipation of the atoms and molecules has been overseen.

Since also for the elastically reflected atoms and molecules a cosine distribution is observed we have to state that only the momentum and not the energy of these particles is transferred to the target.

With our obtained result it also seems possible that the reflection coefficient for the intermediate energy range of some eV can be interpolated between 30 eV D^+ results and the thermal D^0 , whereby the acceleration of

the low energetic ions in the ion-surface potential up to their neutralization has to be taken into account.

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