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1 **TALIF measurements of hydrogen and deuterium surface loss**
2 **probabilities on quartz in low pressure high density plasmas**

3 X. Yang,^{1,2,*} D. Kogut,¹ L. Couëdel,^{1,3} T. Angot,¹

4 P. Roubin,¹ J.-B. Faure,¹ and G. Cartry^{1,†}

5 ¹*Aix-Marseille Université, CNRS, PIIM,*

6 *UMR 7345, Centre Scientifique de Saint Jérôme,*

7 *case 241, 13397 Marseille Cedex 20, France*

8 ²*Institute of Plasma Physics, CAS,*

9 *Shushanhu road 350, Hefei, Anhui, 230031, China*

10 ³*Department of Physics and Engineering Physics,*

11 *University of Saskatchewan, Saskatoon, SK S7N 5E2, Canada*

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Abstract

13

14 This article deals with surface loss on quartz of atomic hydrogen (H) and its isotope deuterium
15 (D) in a low-pressure (10 Pa) pulsed inductively coupled plasma. The atomic temporal decay in the
16 post discharge is measured by Two-photon Absorption Laser-Induced Fluorescence (TALIF). From
17 the loss rate, the atomic surface loss probability is determined. In pure hydrogen or pure deuterium
18 gas, no isotopic effect on surface kinetics has been observed and the surface loss probabilities of
19 H and D were found to be almost identical and equal to $\sim 1.8\%$. However, despite the lack of
20 difference in surface loss probability, a net isotopic effect on surface loss rate due to the mass
21 difference between the isotopes is measured. Hydrogen atoms diffuse faster and have higher flux to
22 the plasma chamber walls than deuterium atoms. Hydrogen atoms are therefore lost at higher rate
23 than deuterium atoms. Based on the observed isotopic difference and on the comparison between
24 H and D TALIF signals, the isotopic effects on H and D atom production are discussed.

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26 I. INTRODUCTION

27 In low-pressure plasma sources, due to low collisionality and fast diffusion, the surface
28 chemistry on the reactor walls in contact with the plasma plays a major role on the plasma
29 equilibrium [1]. Radical densities depend on chemical reactions at the wall rather than
30 reactions in the plasma volume. This surface chemistry leads to complexity in industrial
31 plasma processes, such as those employed in the microelectronics industry, because surface
32 state must be controlled perfectly to obtain reproducible results. This issue is usually fixed
33 by employing systematic wall conditioning procedure before any process [1]. Nevertheless,
34 the radical densities in the plasma are set by wall reactions, the rate coefficients of which
35 are poorly known, preventing efficient development support from plasma modelling. Even in
36 simple chemistry, when using gases such as oxygen, hydrogen, nitrogen, surface chemistry is
37 a key issue as it determines directly the concentration of the active atomic species. The loss
38 of atomic species at the wall, whether through sticking or recombination into molecules, is
39 hard to predict theoretically because it strongly depends on the surface state which in turn

* xin.yang@ipp.ac.cn

† gilles.cartry@univ-amu.fr

40 is depending on the plasma conditions through the ion flux towards the wall, the energy of
41 ions impinging the wall, the atomic flux, etc. As a consequence, the surface loss probability,
42 which is the probability for an atomic species to be lost by any mechanism when hitting the
43 wall, is often used as a fitting parameter in models. The best solution, when possible, is to
44 measure it in-situ, in the plasma source of interest. The goal of this article is to determine
45 the hydrogen and deuterium atomic loss on plasma quartz walls in a low pressure high
46 density inductively coupled plasma source.

47 Hydrogen atom (H) surface losses in low-pressure plasma is of interest for many applica-
48 tions such as plasma etching in microelectronics, surface cleaning, etc. Deuterium atom (D)
49 surface losses in low-pressure plasma are of interest in the context of magnetically confined
50 fusion plasmas. In tokamaks (magnetic confinement fusion reactors) surface reactions of
51 hydrogen/deuterium atoms at reactor walls affect the fuelling efficiency, the plasma den-
52 sity control and the density of neutral hydrogen at the plasma boundary, which impacts
53 particle and energy transport [2]. Atomic surface reactions in tokamaks refer to retention
54 (sticking on the surface or introduction of hydrogen inside the wall volume) and recycling
55 (formation of molecules at the wall). Recycling of hydrogen atoms forming molecules di-
56 rectly impacts the plasma edge composition and is of primary importance in the so-called
57 detached plasma regime [3] which is targeted for ITER operation [4]. The ultimate goal of
58 our research program is to measure atomic losses at the surface of fusion relevant materi-
59 als (tungsten as a priority, but also tungsten nitrides, stainless steel, etc). To this end, a
60 low pressure plasma source has been specially developed [5]. It consists of an inductively
61 coupled plasma confined by quartz walls interacting with a sample made of the material of
62 interest, and equipped with Two photon Absorption Laser Induced Fluorescence (TALIF)
63 diagnostics. TALIF measurements give access to surface loss probabilities. As surface loss
64 probabilities depend on plasma conditions and may vary from one source to another, the
65 objective is mostly to give trends such as variations induced by the type of material, surface
66 temperature, ion flux, etc. As a first step, atomic losses on quartz need to be determined
67 since quartz is the main wall material of our plasma source. In the present article, H and D
68 atomic loss probabilities on quartz are determined using time resolved TALIF measurements
69 in pulsed (10 Hz) hydrogen/deuterium plasmas. In the plasma post-discharge, no molecular
70 dissociation occurs anymore and the atomic decays measured by TALIF are directly related
71 to surface loss.

72 The first part of the article presents the experimental set-up and describes the TALIF
73 diagnostic system. Details on TALIF calibration are given. In the second part, time resolved
74 TALIF measurements in pure H₂, pure D₂ and in H₂ : D₂ mixtures are presented. Surface
75 loss probabilities are then calculated. Finally, the results are discussed.

76 II. EXPERIMENTAL SET-UP

77 A. Plasma chamber

78 The plasma reactor (see Figure 1) is composed of a stainless steel spherical plasma cham-
79 ber (30 cm in diameter) with a top quartz window (166 mm in diameter, 12 mm thick)
80 allowing for RF power coupling between an external three turns planar coil antenna and
81 the plasma. A temperature controlled sample holder of 145 mm diameter is placed oppo-
82 site the quartz window at a distance of 149 mm. It is associated to a load-lock system for
83 fast introduction under vacuum of 10 cm sample wafers. This sample holder is designed to
84 study atomic surface loss probabilities on various materials. However, in the present study,
85 a quartz disc (172 mm diameter and 3 mm thickness) has been installed on top of the sam-
86 ple holder and fully covers it. The plasma region is radially limited by a cylindrical quartz
87 tube (160 mm internal diameter, 5 mm thickness and 140 mm height) placed between the
88 bottom quartz disc and the top quartz window. The plasma is therefore almost completely
89 surrounded by quartz walls. Only a 5 mm height gap remains between the lateral quartz
90 tube and the quartz top window to allow for gas pumping, as well as a small 1 mm gap
91 between the cylinder tube and the bottom quartz disc.

92 The plasma chamber is equipped with one ionisation gauge (54132-GE02 Granville
93 Phillips) to measure the base pressure ($\sim 2 \cdot 10^{-6}$ Pa) and MKS 121A capacitance Baratron
94 gauge to monitor the pressure during plasma operation. Both of them are attached on the
95 flanges of stainless steel chamber containing the quartz tube. The vacuum is ensured by Var-
96 ian Turbo-V551 turbo molecular vacuum pump and an Alcatel oil rotary pump. Ultra-high
97 purity gases (UHP 99.99) are introduced into the vacuum vessel through Brooks mass flow
98 controllers 5850TR series from a top side window. Krypton, used for TALIF calibration,
99 was introduced using a mini gas cylinder. During plasma operation, the pressure was regu-
100 lated by an adjustable gate valve placed between the turbo molecular pump and the plasma

101 chamber. The total gas flow was set at 20 sccm, both for pure gas or gas mixture operation.
 102 Under these conditions, gas residence time in the plasma chamber, without considering the
 103 presence of the quartz tube, is estimated to be of the order of 10 seconds.

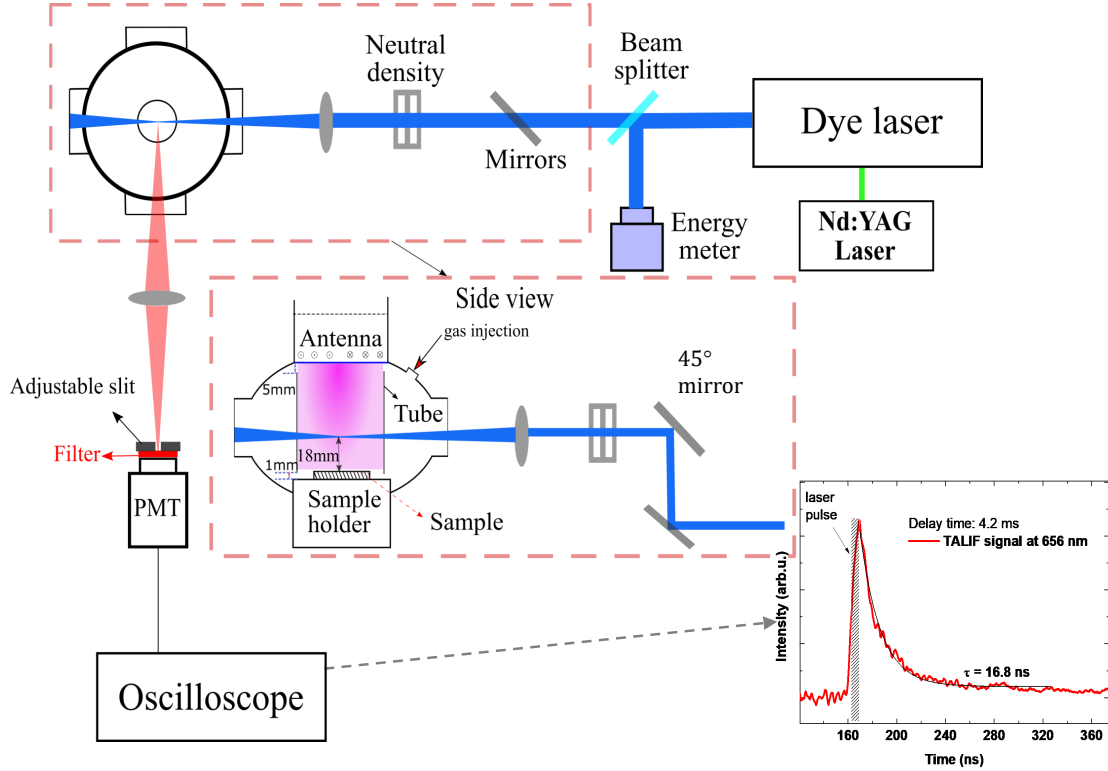


FIG. 1. Schematic of the experimental set-up. The inset shows an example of the evolution of the TALIF signal as a function of time

104 Pulsed Inductively coupled plasma (ICP) was used in this work to investigate plasma-
 105 surface interaction. Inductive coupling was obtained thanks to a three turns planar coil
 106 antenna placed on top of the quartz window. It is made of copper tube (6 mm diameter)
 107 cooled by internal water circulation. The outside termination of the antenna was connected
 108 to ground through a variable capacitor used to decrease the voltage at the antenna termi-
 109 nation and to limit capacitive coupling [6]. Using high voltage probes, its value was set to
 110 ensure a virtual ground on antenna's location. The inner termination of the antenna was
 111 connected to a CesarTM 1310 Radio Frequency generator through a L-type matching box
 112 containing two variable capacitors. The two capacitors were adjusted to ensure impedance
 113 matching under different discharge conditions. The RF match box was first manually tuned
 114 to minimise the reflected power with steady plasmas. Then, with pulsed plasmas, the match-

115 ing was improved by fine tuning of the capacitances based on real time monitoring of the
 116 electron density n_e by a microwave interferometer. A Ka-band Microwave Interferometer
 117 (MWI 2650-A) was used. The operating frequency of our microwave interferometer is 26.5
 118 GHz and its measurement range is from $\sim 10^{16} - 10^{17} \text{ m}^{-3}$. The microwave line of sight was
 119 passing through the inner quartz tube just above the sample (quartz disc at bottom), and
 120 two opposite 38 mm diameter view ports.

121 The working pressure was set to 10 Pa as plasma re-ignition in pulsed mode is harder at
 122 lower pressure. The input power was set to 1000 W which was the maximum available power.
 123 Lower power led to difficulties for plasma re-ignition in pulsed mode. Pulse frequency was
 124 chosen equal to 10 Hz and the duty cycle was set to a low value(10%). Discharge time t_{on}
 125 was 10 ms and post-discharge time t_{off} was 90 ms. Previous characterisation of the plasma
 126 source shows that 10 ms are long enough to reach a steady-state plasma without increasing
 127 noticeably the average wall temperature at a 10% duty cycle. Wall and sample temperatures
 128 after 40 min of pulsed plasma operation were $\sim 40^\circ\text{C}$ as measured by a thermocouple. Finally,
 129 a 30 min long continuous wave (CW) plasma under capacitive mode with input power of 200
 130 W was applied for wall conditioning purpose before each series of TALIF measurements. A
 131 Pyrex tube with a hole was used to introduce at the centre of the plasma a RF compensated
 132 Scientific System Langmuir probe 5 cm above the bottom quartz disc. Electron density and
 133 electron temperature measured at the end of the pulse are respectively $n_e = 9 \cdot 10^{16} \text{ m}^{-3}$
 134 and $T_e = 0.7 \text{ eV}$ giving an estimated positive ion flux onto the surfaces of $\sim 10^{20} \text{ m}^{-2}\text{s}^{-1}$.

135 B. TALIF measurements

136 Atomic H and D measurements were carried out by TALIF. Atomic H in its ground state
 137 ($1s \ ^2S_{1/2}$) was excited by simultaneous absorption of two laser photons, with a wavelength of
 138 205 nm (205.1445 nm for H atoms and 205.0876 nm for D atoms), to the excited electronic
 139 levels $3s \ ^2S_{1/2}$ and $3d \ ^2D_j$. Excited states relaxed by spontaneous emission of a Balmer- α
 140 photon at 656.3 nm from the $3d \ ^2D_j$ and $3s \ ^2S_{1/2}$ state to the $2p \ ^2P_j$ state. Since the two-
 141 photon absorption cross section for $1s \rightarrow 3d$ transition is 7.56 times higher than for $1s \rightarrow 3s$
 142 transition [7], the $3d \rightarrow 2p$ transition dominated the de-excitation. The fluorescence decay
 143 time which is related to the lifetime of the excited state for $3d \ ^2D_j$ is 15.5 ns [7]. Krypton
 144 gas is often employed for absolute calibration of H density measured by TALIF [8] due to its

145 similar two-photon absorption scheme. It has been used here for calibration and comparison
146 purposes. Krypton (Kr) in the ground state $4p^6\ ^1S_0$ was excited to $5p'[3/2]_2$ excited state
147 by two photon absorption at 204.2 nm. The fluorescence to the $5s'[1/2]_1$ state was observed
148 at 826 nm. The natural lifetime for the excited state of krypton ($5p'[3/2]_2$) is 35 ns [9].

149 The second harmonic wavelength (532 nm) of a Continuum's Surelite III Nd:YAG laser
150 (~ 6 ns pulse, 10 Hz) pumped a NarrowScan dye laser whose output delivered wavelength
151 at 615 nm in a ~ 10 ns pulse. The required 205 nm wavelength was generated by frequency
152 doubling and frequency mixing with nonlinear crystals, with an output laser energy of about
153 1 mJ/pulse.

154 Figure 1 shows a schematic of TALIF experimental system. The laser beam was guided
155 to the plasma chamber through two parallel mirrors (25.0 mm 193 nm 45° , excimer Laser
156 Line Mirror, Go Edmund) with a 45° angle of incidence. A series of neutral density filter
157 mounted on a manual filter wheel station was positioned on the way of the laser beam to
158 adjust the laser energy entering the plasma chamber. Then the laser beam was focused by
159 an $f = 30$ cm plano-convex suprasil spherical lens at the centre of the plasma chamber and
160 injected into the plasma chamber through a fused-silica optical access window. In order to
161 decrease the laser beam reflection and diffusion on the quartz tube and increase the laser
162 intensity to the measurement position, a 5 mm diameter hole was drilled on the pathway of
163 the laser beam on one side of the tube. The laser beam passes through the chamber parallel
164 to the surface of the quartz bottom disc at a distance of 25 mm above it. The fluorescence
165 detection was performed perpendicularly to the laser beam through the quartz tube and a
166 common view port. The spectral selection was achieved by an interference filter centred at
167 655 nm for atomic H with 40 nm bandwidth (Semrock, FF01-655/40) or centred at 842 nm
168 for Kr with 56 nm bandpass (Semrock, FF01-842/56). An adjustable slit was placed in front
169 of the filter to control the light flux. The slit was oriented perpendicular to the laser beam.
170 The fluorescence photons passing through the slit were detected by a side-on Hamamatsu
171 9110 photomultiplier tube (PMT). A gated operation of PMT was required since the strong
172 emission signal of the background plasma pulse was saturating the PMT and was preventing
173 any measurement in the early post discharge. A "normally off" Hamamatsu C1392-56 gated
174 socket assembly was used with a gate duration of 10 μ s. The PMT output was recorded
175 with an oscilloscope (LeCroy WaveSurfer 64MXs-B) through a 50 Ω input impedance for
176 current-to-voltage conversion and was then sent to a computer for data processing. The

177 laser energy for each individual pulses was monitored by a power & energy meter (SOLO
178 2, Gentec-EO, Canada) and recorded directly on a computer thanks to a data acquisition
179 board.

180 A waveform generator delivering TTL signals at 10 Hz was used as master clock to
181 synchronise the laser shot, the plasma pulse, the gated PMT signal, the laser energy mea-
182 surement, and the TALIF signal acquisition, using several delay generators. Despite the
183 fact that plasma pulse ignition was ensured at 10 Pa, plasma pulse reproducibility was not
184 perfect and could impact the quality of TALIF measurement in the early afterglow. The
185 issue was solved by monitoring in real time electron density during the plasma pulse with the
186 microwave interferometer. According to some thresholds in pulse duration and electron den-
187 sity values, the pulse was qualified or not for TALIF measurement. In the same way, the RF
188 forward power related signal given by the RF generator was also used as a third condition for
189 pulse qualification. A homemade electronic circuit was generating a TTL signal triggering
190 the scope acquisition when all qualification requirements were met. This scheme enabled to
191 collect a subset of pulses with good reproducibility to make reliable TALIF measurements.
192 It is presented in details in Ref. [10].

193 The absorption line profiles were scanned and the relative densities of atomic hydrogen
194 and deuterium in the post-discharge were evaluated by calculating the area under the curve.
195 In order to ensure constant laser energy during scans, lookup tables of laser energy versus
196 laser wavelength were previously established and used during the measurements.

197 Qualified TALIF signals were recorded with the oscilloscope working under ‘sequence’
198 mode. Under this mode, the TALIF signal was recorded pulse-by-pulse by the scope and
199 stored in the internal memory. Typically, a sequence was made of 20 wavelengths and 50
200 trigger events for every wavelength. The output file contains 1000 fluorescence signals for
201 one delay time acquired in a reasonable time of about 5 to 10 minutes. For data processing,
202 the averaged TALIF signal at a given wavelength was normalised by the square of the
203 corresponding averaged laser energy. The normalisation was performed automatically by a
204 homemade routine.

205 1. *Transition saturation*

206 Compared to single-photon LIF, TALIF presents a quadratic dependence of the signal to
207 the laser energy. At low laser energy, the TALIF signal is proportional to the ground-state
208 atom density and the square of the laser energy. On the contrary at high laser energy,
209 additional depopulation pathways of $n = 3$ level, such as multi-photon ionisation by a third
210 photon absorbed [11] and two-photon-excited stimulated emission (TALISE) [12], start to
211 compete with the radiative depopulation. To ensure that these depopulation pathways did
212 not affect the results, the incident laser energy was varied using neutral filters and TALIF
213 signals were recorded at constant atom density. Figure 2 shows typical results for Kr and
214 H. For Kr measurements, the plasma chamber was filled at a pressure of 10 Pa. For atomic
215 H and D, measurements were performed in the post-discharge plasma with two delay times
216 of 0.05 ms and 4 ms, which respectively represented high and low atomic density. TALIF
217 signal as a function of laser energy is plotted in Figure 2. The exponents s of the polynomial
218 parts are between 1.74 and 1.99 for all measurements, close to the expected value of 2 for a
219 quadratic dependence of the TALIF signal with respect to the laser energy. The saturation
220 threshold for krypton was around 30-40 μJ . The TALIF signal of H and D atom remained
221 in the non-saturated regime over the entire scanned range of laser energy (up to 370 μJ
222 routinely obtained, somewhat lower than the maximum output of the dye laser 1 mJ due
223 to losses in the beam splitter and optics and possibly to non optimised dye laser tuning).
224 Measurements were then performed with a 370 μJ laser energy for H and D.

225 2. *Photomultiplier saturation*

226 For reliable measurements, the PMT must be used in its linear regime where the relation-
227 ship between the incident light level and the anode output current is linear. Space charge
228 limitation of the anode current was observed even at moderate TALIF signal intensity due
229 to the high employed gain of the PMT. In order to maintain linearity over a broader range
230 of TALIF signal intensity, a so-called ‘tapered voltage-divider’ circuit was inserted in the
231 measurement circuit. The electric field between the last dynode and the anode of the PMT
232 was increased by doubling the resistance of the biasing circuit, thus doubling the voltage
233 drop of this last dynode stage. More details can be found in Yang’s thesis [10]. In the

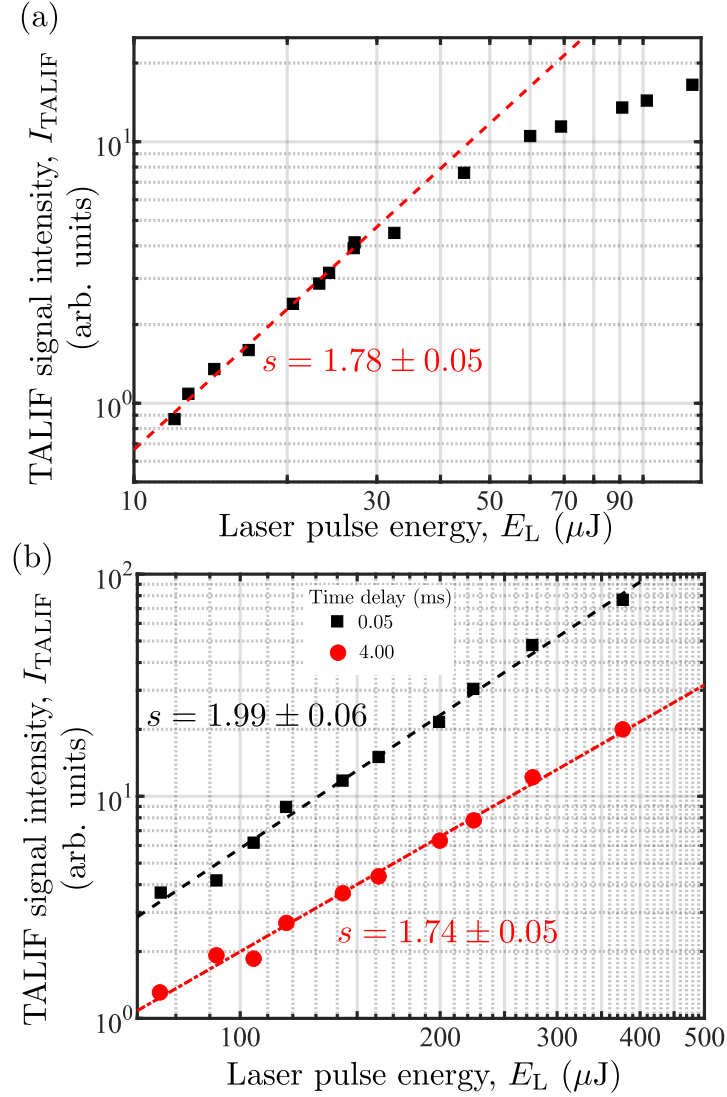


FIG. 2. TALIF signal intensity I_{TALIF} as a function of laser pulse energy E_L : (a) Kr at 10 Pa, and (b) hydrogen in H_2 plasma, 10 Pa, 1000 W, for two time delays in the post discharge (0.05 ms and 4 ms). The exponents s were obtained by fitting the experimental data with a function of the form $I_{\text{TALIF}} = A \cdot E_L^s$.

234 absence of PMT space charge saturation, the decay time of the TALIF signal should be
 235 the natural lifetime of the excited state (15.5 ns and 35 ns for H and Kr respectively) since
 236 non radiative decay or line trapping are negligible in the present experimental conditions.
 237 If the anode current is saturated, the anode current intensity is no more proportional to
 238 the incident light level and the decay time of the TALIF signal becomes smaller than the
 239 natural lifetime. Fluorescence signals from Kr and atomic H were recorded. Figure 3 shows

240 the results of these measurements. Kr pressure of 23.7 Pa and 18.5 Pa were used for the
241 measurements without and with the voltage-diver circuit, respectively. It is worth noting
242 that a higher laser energy ($\sim 80 \mu\text{J}$, outside the quadratic dependence region) had to be set
243 to demonstrate PMT saturation with Kr while PMT saturation was observed for H in the
244 quadratic dependence region. H measurements were performed at a time $t = 0.2 \text{ ms}$ in the
245 post discharge. An exponential fit of the data, excluding the laser pulse duration ($\sim 10 \text{ ns}$),
246 was performed in order to get TALIF decay times as a function of the PMT slit opening.
247 An example of fluorescence measurements and the fitting results are shown in Figure 3. By
248 increasing the slit opening, the incident light flux onto the PMT was increased. As shown in
249 Figure 3 (a and b), the intensity of TALIF signal was increased and the decay time remained
250 at a constant value, close to the theoretical one, unless the incident light flux was too high
251 leading to the saturation of the PMT signal. Based on the observed increase of the decay
252 time at high photon flux (Figure 3b), the saturation started when using the 'non-tapered
253 voltage-divider' when the slit opening was about $20 \mu\text{m}$ corresponding to a measured volt-
254 age in the range $120 - 200 \text{ mV}$. It means that under these conditions, the TALIF signal
255 should be maintained below $120 - 200 \text{ mV}$ by reducing the incident light level. This was
256 limiting the measurement over a relatively small range of intensity and prevents measuring
257 low atomic hydrogen density in the late post-discharge. Figure 3b shows that the PMT sat-
258 uration threshold when using the 'tapered voltage-divider' circuit was reached at a higher
259 photon flux with a slit opening between 80 and $160 \mu\text{m}$, corresponding to about $\sim 500 \text{ mV}$
260 (PMT saturation is shown by gray ellipse on Figure 3a). The PMT linearity range was thus
261 improved and higher TALIF signal intensity could be recorded, thus improving signal-to-
262 noise ratio and atomic detection limit.

263 3. *Absolute density calibration*

264 In order to obtain absolute density, the technique proposed by Goehlich et al [13] was
265 used. The method is based on a comparison between the TALIF signal of the studied atomic
266 species with the TALIF signal of a noble gas which has a two-photon resonance spectrally
267 close to the transition investigated. A prerequisite for its applicability is that both TALIF
268 excitations are performed with identical spatial, spectral, and temporal intensity distribution
269 of the laser radiation. This removes the necessity of knowing the intensity distribution

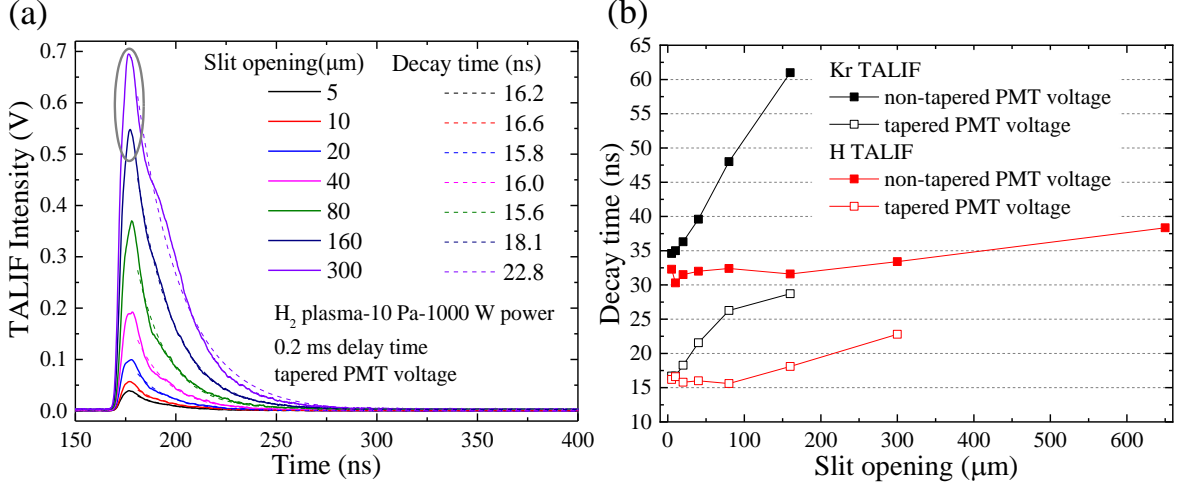


FIG. 3. (a) H TALIF signals versus slit opening (i.e versus photon flux) using a ‘tapered voltage-divider’ for the PMT dynode biasing. Appearance of PMT saturation is shown by the grey ellipse and is determined based on the measurement of TALIF decay times. (b) Kr and H TALIF decay times versus slit opening with and without a ‘tapered voltage-divider’ for the PMT dynode biasing. Krypton measurements were performed at ~ 20 Pa without plasma. Hydrogen measurements were performed in a 1000 W, 10 Pa, 10 Hz pulsed plasma with a time delay $t = 0.2$ ms.

270 explicitly. The condition is best fulfilled if the two-photon resonances are spectrally as close
 271 as possible. For this reason, Kr was employed. The ratio of Kr to H TALIF signal intensities,
 272 $I_{\text{TALIF,Kr}}/I_{\text{TALIF,H}}$ is given by:

$$273 \quad \frac{I_{\text{TALIF,Kr}}}{I_{\text{TALIF,H}}} = \gamma \frac{n_{\text{Kr}} \sigma_{\text{Kr}}^{(2)}}{n_{\text{H}} \sigma_{\text{H}}^{(2)}} \left(\frac{I_{0,\text{Kr}} \lambda_{\text{Kr}}}{I_{0,\text{H}} \lambda_{\text{H}}} \right)^2 \frac{a_{32,\text{Kr}}}{a_{32,\text{H}}}, \quad (1)$$

274 where γ is the detection efficiency ratio for the two observed fluorescence wavelengths, n
 275 is the atom density, σ is the two photon absorption cross section, λ is the wavelength,
 276 I_0 is the laser energy, and a_{32} is the branching ratio of the fluorescence channel. The
 277 detection efficiency ratio γ between photon at 656 nm (H atom) and 826 nm (krypton)
 278 was determined using a blackbody (Luminance Radiance Standard from SphereOptics).
 279 Measurements resulted in a ratio equal to 0.73 ± 0.02 .

280 For a gas at very low pressure and short lifetime excited states, no collisional deactivation
 281 occurs and the branching ratio a_{32} can be written as $a_{32} = A_{32} \cdot \tau_3$, where A_{32} is Einstein
 282 coefficient, τ_3 is the natural lifetime. The H atom density is then given by:

$$283 \quad n_{\text{H}} = \chi \frac{I_{\text{TALIF,H}}}{I_{\text{TALIF,Kr}}} \cdot \left(\frac{I_{0,\text{Kr}}}{I_{0,\text{H}}} \right)^2 n_{\text{Kr}}, \quad (2)$$

284 where the factor χ is only composed of atomic and experimental constants,

$$285 \quad \chi = \gamma \frac{A_{32,\text{Kr}} \tau_{3,\text{Kr}} \cdot \sigma_{\text{Kr}}^{(2)} \cdot \lambda_{\text{Kr}}^2}{A_{32,\text{H}} \tau_{3,\text{H}} \cdot \sigma_{\text{H}}^{(2)} \cdot \lambda_{\text{H}}^2}. \quad (3)$$

286 The ratio of the two-photon excitation cross sections was measured by Niemi et al [8]
 287 and the value is $\sigma_{\text{Kr}}^{(2)}/\sigma_{\text{H}}^{(2)} = 0.62$. Table I summarises the values of all parameters involved
 288 in the H atom density calibration via a Kr TALIF signal.

TABLE I. Parameters involved in the atomic hydrogen density calibration via krypton.

| | Kr | H |
|------------------------------|-----------------------|------------------------|
| λ (nm) | 204.1954 | 205.1445 |
| A_{32} (s^{-1}) | $2.4 \cdot 10^7$ [14] | $6.45 \cdot 10^7$ [15] |
| τ (ns) | 35.4 [9] | 15.5 [7] |
| γ | | 0.73 |
| χ | | 0.43 |

289 For calibration, Kr was injected into the plasma chamber at three different pressures and
 290 excited with a laser energy of $31 \mu\text{J}$. The detection system for krypton was identical as for H
 291 atom, except for the laser energy that was set to $376 \mu\text{J}$ for H. Relative H atom density decay
 292 in 10 Hz, 10 % duty cycle, 1000 W input power, H_2 plasma was then calibrated (Figure 4).
 293 At the moment of the calibration, an alumina sample was installed in the chamber instead
 294 of the quartz sample. The sample material could affect the atomic density when compared
 295 to the full quartz situation, but the order of magnitude obtained here are still comparable
 296 to previous measurements realised in steady state plasma [5] since the sample surface was
 297 relatively small compared to surface area of the rest of the chamber walls. The absolute
 298 atom density at a time delay of 0.05 ms was $(9 \pm 1) \cdot 10^{19} \text{ m}^{-3}$. The absolute atom density
 299 in this experimental set-up and at the same pressure and RF power but in steady state was
 300 also determined by Ar actinometry with H_β line in $\text{H}_2 + 5\% \text{ Ar}$ plasma using a Pyrex tube
 301 instead of a quartz one (Figure 14 of reference [5]). The result was $\sim 2.5 \cdot 10^{20} \text{ m}^{-3}$ which
 302 compares quite well in term of order of magnitude to the present experiment given the slight
 303 differences between the experimental conditions (Pyrex tube instead of quartz tube, quartz
 304 sample instead of alumina sample, introduction of 5% argon, etc).

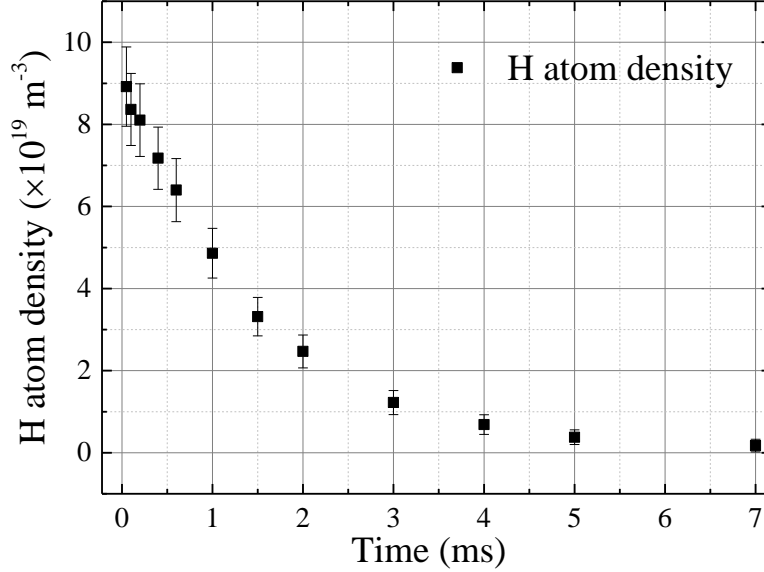


FIG. 4. Absolute H atom density in the post-discharge (10 Pa, 10 Hz, 10% duty cycle, 1000 W input RF power, pure H₂ plasma, 376 μ J laser energy)

305 4. *Laser line width calibration*

306 Figure 5a and b show the TALIF measured absorption profile for H and D atoms at
 307 different time delays, as well as the corresponding recorded laser energy. Each data point is
 308 an average of 50 TALIF signals normalised by the square of the average of the corresponding
 309 50 recorded laser energies. The error bar of each point results from the standard deviation
 310 of the 50 averaged measurements. The solid curve is a Gaussian fit curve. The width of
 311 the Gaussian line is determined by the convolution of the Doppler broadening ($\Delta\lambda_D$) given
 312 by the atomic temperature and the laser line width ($\Delta\lambda_L$). H and D absorption profile full
 313 width at half maximum (FWHM) are given by:

314
$$\Delta\lambda_m^2 = \Delta\lambda_D^2 + \Delta\lambda_L^2 \quad (4)$$

315 The laser line width is 1.2 pm at 615 nm (0.03 cm^{-1}) from manufacturer specifications
 316 giving a theoretical width of $\sim 0.4 \text{ pm}$ at 205 nm (0.09 cm^{-1}). Using this laser line width
 317 leads to H and D temperature in the late post discharge higher than 1000 K and well above
 318 the expected value of 300 K (wall temperature remains close to room temperature). It
 319 shows that the laser was spectrally broader than expected preventing atomic temperature
 320 measurements unless laser line width was properly calibrated. Such an issue was already

321 reported in [16].

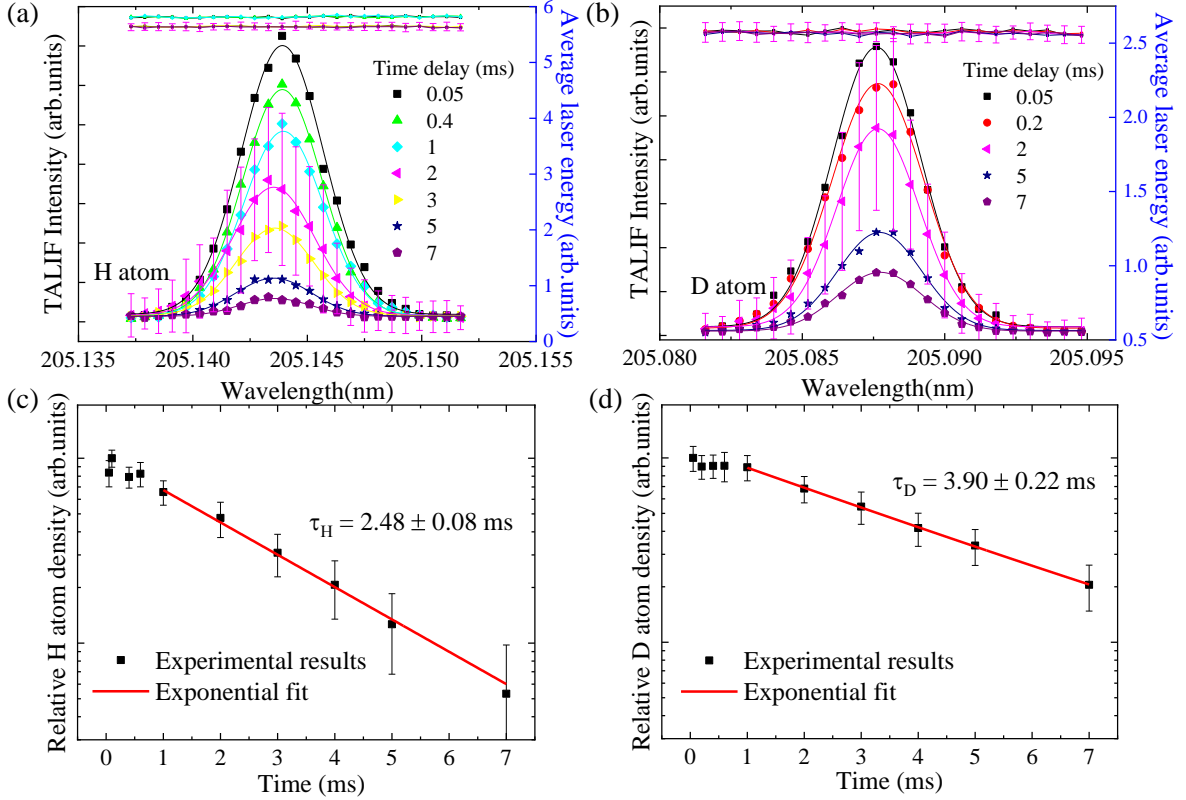


FIG. 5. TALIF measurement of H atom and D atom densities in 10 Pa, 10 Hz, 10% duty cycle, 1000 W input RF power H_2 (D_2) plasmas. The laser pulse energy recording during measurement is shown above the profiles (laser energy is about $370 \mu\text{J}/\text{pulse}$). (a) and (b) show the excitation spectrum at different time delays. (c) and (d) show the relative atom density as a function of time in the post discharge together with an exponential fit of the data. In (a) and (b), in order to avoid overlapping, the error bars are only shown for one time delay. The error bars correspond to the error of 50 averaged measurements for each wavelength.

322 Krypton is 42 times heavier than hydrogen and presents a narrow Doppler broadening
 323 at room temperature (~ 0.27 pm) which is smaller than the laser (theoretical or real) line
 324 width. Its absorption profile should theoretically give the laser line width. However, the
 325 absorption profile measured by TALIF with a laser energy of $30 \mu\text{J}$ at low pressure was
 326 found to be quite large (~ 2.7 pm, not shown here) and was probably broadened by multiple
 327 transitions coming from sub-levels and/or isotopic shifts. Two other methods were thus used
 328 to determine laser line width.

329 The first one was proposed by Lamara et al [17]. It consists in measuring the absorption
330 line of H and D atoms in discharges in H₂/D₂ mixture (see an example in Figure 8). H and
331 D atoms are supposed to be in thermal equilibrium. Their excitation laser wavelengths are
332 very close, and this gives the advantage of doing both absorption profile measurements with
333 nearly identical laser properties. As H and D absorption profiles depend on the same two
334 unknown parameters, the atomic temperature (assumed to be equal for H and D) and the
335 laser line width, they can now be determined.

336 The absorption spectra of atomic hydrogen and deuterium in 50% H₂ + 50% D₂ plasma
337 were recorded. The plasma was operated at 10 Pa, 10 Hz, 10% duty cycle, and 1000 W input
338 power. Measurements were done with different laser energies at different time delays in the
339 post-discharge (and thus different atomic temperatures). The normalised TALIF profiles
340 were fitted with Gaussian functions in order to get the FWHM $\Delta\lambda_{mH}$ and $\Delta\lambda_{mD}$ from which
341 the laser line width was determined. The deduced averaged laser apparatus function was
342 1.76 ± 0.1 pm. The uncertainty includes a contribution from the Gaussian fit accuracy and
343 a contribution from the reproducibility of the experiment. The obtained value was lower
344 than that obtained by krypton excitation spectrum (~ 2.7 pm).

345 In order to confirm the laser line width measured by the above method, a second method
346 consisting in scanning the absorption spectrum of NO molecule at 205 nm was used. The NO
347 molecule has ro-vibrational transitions between $A^2\Sigma$ and $X^2\Pi$ electronic state [18]. The
348 single-photon absorption spectrum of NO molecule at room temperature was measured. For
349 laser line width calibration, we have selected a transition with excitation wavelength and
350 fluorescence at 205.28 nm ($A^2\Sigma^+(\nu = 2) \rightleftharpoons X^2\Pi(\nu = 0)$). The gas introduced in the vessel
351 was a mixture of 99% Ar and 1% of NO. The gas pressure was set at 50 Pa which means the
352 NO partial pressure was 0.5 Pa. Since the cross section is much higher for the single photon
353 excitation than for the two-photon excitation, the laser injection was operated here without
354 focusing. The fluorescence was focused on the photo-multiplier without any optical filter.
355 The laser was scanned from 205.2802 nm to 205.2640 nm. The laser energy was 14 μ J. Due to
356 its large mass, the Doppler broadening of NO molecule at room temperature is small (~ 0.46
357 pm) and cannot be resolved by the laser (theoretical bandwidth of 0.4 pm). Therefore, the
358 Doppler broadening can be neglected and the line broadening of the excitation spectrum is
359 related to the laser apparatus function (laser line width). Figure 6 shows the absorption
360 profile of the selected NO transition. It was actually impossible to fit it by either a Gaussian

361 function, nor by the convolution of a Gaussian (FWHM 0.46 pm) with a Lorentzian. Only
362 a Lorentzian function was able to fit correctly the spectrum.

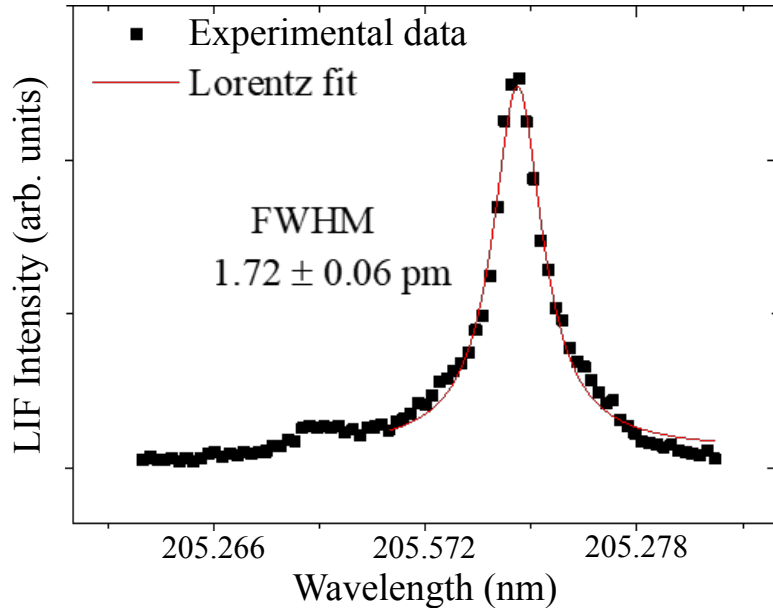


FIG. 6. Absorption spectrum of NO and corresponding fit by a Lorentz function. The laser pulse energy was $14 \mu\text{J}$, the laser wavelength was scanned from 205.2622 nm to 205.2462 nm, by steps of 0.0002 nm, 80 trigger events per step

363 The Doppler broadening was neglected and it was assumed that the Lorentzian width
364 obtained is the laser line width. The deduced laser broadening was $1.72 \pm 0.06 \text{ pm}$ which
365 agrees very well with the broadening obtained from the H and D scan. This confirmed that
366 the laser line width was around 1.7 pm at 205 nm.

367 Using this value for the laser line width, time resolved measurements of the atomic tem-
368 perature by performing Gaussian fits of the absorption profiles were possible. The atomic
369 temperature was observed to decrease rapidly during the first millisecond of the post dis-
370 charge. However the errors on the temperature measurement were rather large and fluc-
371 tuations up to $\sim 100 \text{ K}$ were observed. The reasons behind these observed temperature
372 fluctuations are still unknown. Possible explanations are small changes of the laser line
373 width with time and insufficient averaging resulting in a decrease accuracy of the Gaussian
374 fits. Despite these fluctuations, it can still be deduced from the measurements that atomic
375 temperatures are more or less in thermal equilibrium with the walls ($\sim 300 \text{ K}$) after about 1
376 ms in the post discharge. One representative measurement is given in Figure 7.

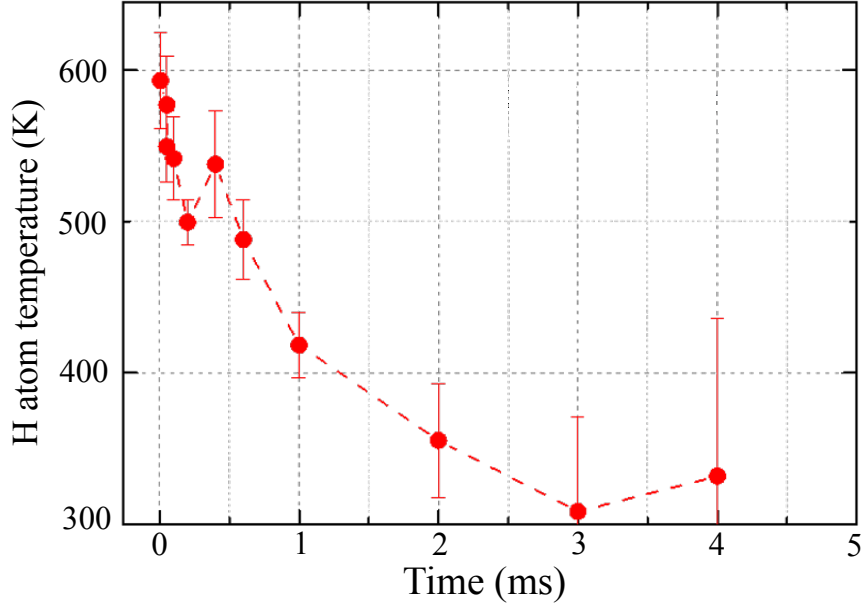


FIG. 7. H atom temperature decay in the post-discharge. Pure H₂ plasma pulsed at 10 Hz, 10% duty cycle and 1000 W input power.

377 III. RESULTS AND DISCUSSION

378 A. TALIF Measurements

379 The relative density of atomic hydrogen and deuterium in the post-discharge was eval-
 380 uated by calculating the area under the curve of the absorption profile. Figure 5c and 5d
 381 show relative atomic hydrogen and deuterium density in the post discharge. The error bar
 382 was the propagation of errors in Figure 5a and 5b. A decay of atomic density over one order
 383 of magnitude was observed before the signal came into noise. One can see that the signal in
 384 the early afterglow was not following a monotonic decay. This is possibly due to gas cooling
 385 during the first millisecond impacting H radial profile and more generally speaking, neutral
 386 density distribution inside the plasma [19, 20]. Therefore, only data points acquired at time
 387 higher than 1 ms were used to determine surface loss probabilities. If one excludes the first
 388 millisecond, the atomic decays were indeed quite accurately described by an exponential
 389 decay function ($y = y_0 + A_1 e^{(-t/\tau)}$) with a time constant τ lower for H than D ($\tau_H < \tau_D$).

390 In order to compare H atom and D atom surface loss probabilities under the exact same
 391 plasma conditions, H and D atom decay times in the post discharges of H₂-D₂ (50%-50%)
 392 plasma were measured. Figure 8 shows the results. The laser pulse energy was $\sim 270 \mu\text{J}$ for

393 this measurement. If one excludes the first millisecond, the decays were again exponential
 394 with $\tau_H < \tau_D$.

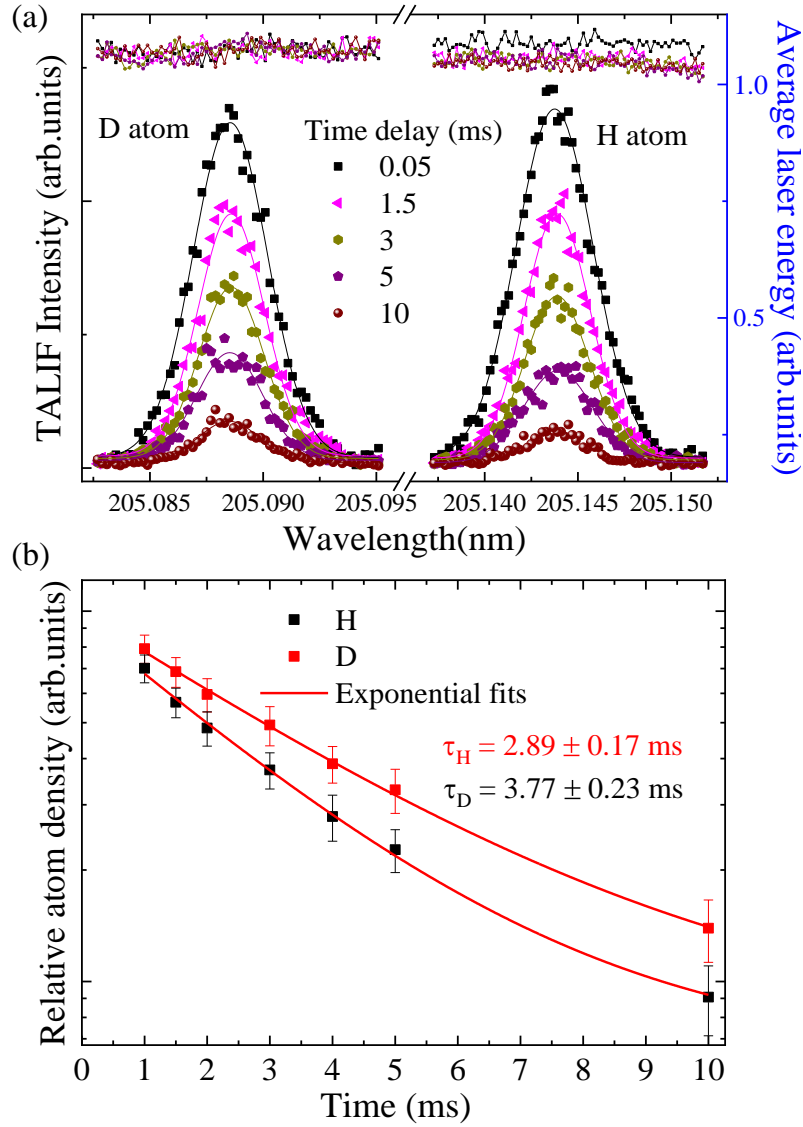


FIG. 8. (a) H and D atom absorption profiles in H_2/D_2 plasmas (1:1 mixture, 1000 W, 10 Pa, 10 Hz, 10% duty cycle) at different times during the post discharge. The laser pulse energy recorded during the measurement of the profiles is shown above the profiles. (b) Relative atom density as a function of time during the post discharge. Fitted lines were obtained using exponential decay functions.

395 H atom decay was also measured in 10 Pa, 1 Hz, 5% duty cycle, 1000 W RF input power
 396 plasmas, for comparison purposes with previous measurements. The laser pulse energy was
 397 $225 \mu J$. Figure 9 shows the TALIF measurements. Excluding the first millisecond, the decay

398 was also exponential.

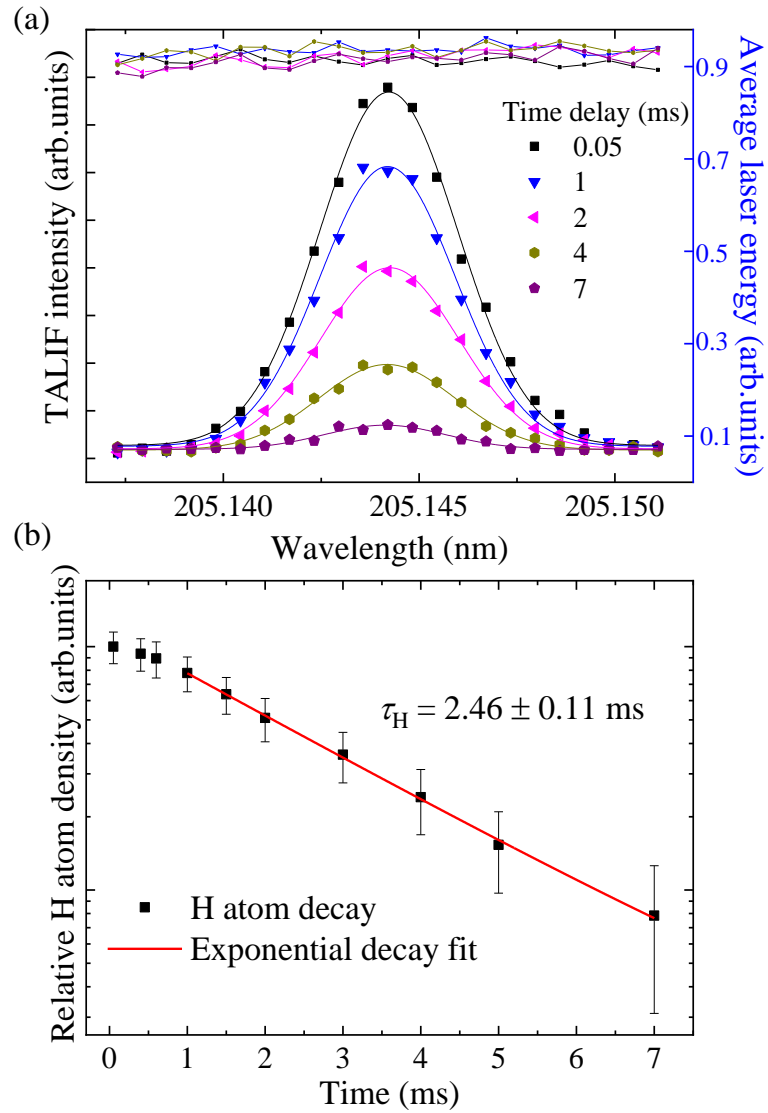


FIG. 9. a) H atom absorption profiles in H_2 plasma (1000 W, 10 Pa, 1 Hz, 5% duty cycle) at different times in the post discharge. The laser pulse energy recorded during the measurement of the profiles is shown above the profiles. (b) Relative atom density as a function of time in the post-discharge. The fitted line was obtained assuming an exponential decay.

399 **B. Surface loss**

400 The H/D atom loss probability on surface was determined from the measurement of the
 401 atom density [H], [D] as a function of time in the post discharge. Atomic reactions on silica

402 like surface are well described in [21]. Briefly, gaseous atoms can be lost at the surface
403 through chemisorption, which is creating and adsorbed atom, direct recombination between
404 a gaseous atom and an adsorbed atom (Eley-Rideal reaction), and recombination between a
405 diffusing atom on the surface and a chemisorbed atom. Eley Rideal process is always a first
406 order process with respect to the gaseous atomic loss (i.e loss rate is proportional to the
407 gaseous atomic density) while Langmuir-Hinshelwood loss can be second order in the limit
408 of low temperature (which is not corresponding to the situation studied in this paper). It
409 is not easy to determine which mechanism is dominating in a given experimental condition
410 but recent measurements in oxygen plasma demonstrated that oxygen atomic loss on Pyrex
411 obviously occurs through the Eley Rideal mechanism at room temperature at least for pres-
412 sure above 100 Pa [22]. For lower pressure the increasing influence of ion bombardment did
413 not permit to conclude on the dominating mechanism. Anyway, for all the reasons men-
414 tioned in this paragraph, it is a reasonable assumption to consider that the atomic surface
415 loss probability is independent on the atomic density giving a first order atomic loss rate as
416 described in the next paragraph.

417 As soon as the plasma pulse is switched off, because of the very fast cooling of the electron
418 temperature, there is no more production of atoms by electron impact. As atomic loss by
419 three body recombination in the plasma volume is much slower than the observed decay
420 time, the equation governing atomic kinetics in the post discharge reads as:

$$421 \quad \frac{\partial[\text{H}]}{\partial t} - D\vec{\nabla}^2[\text{H}] = 0. \quad (5)$$

422 If the diffusion coefficient D is constant in time and space the solution to this equation
423 is an infinite sum of eigenmodes:

$$424 \quad [\text{H}](t, \vec{r}) = [\text{H}]_0 \sum_{i=0}^{\infty} \psi_i(\vec{r}) \exp\left(-\frac{t}{\tau_i}\right). \quad (6)$$

425 The fundamental mode might not describe properly the H atom density spatial profile in
426 a plasma source where significant heating such as the one used in the present study. Indeed,
427 at constant pressure, the “hottest” plasma region might be depleted in neutral atoms [19].
428 However, in the afterglow, it is usually assumed that the H atom density is accurately
429 represented by the fundamental mode since the higher order modes are quickly damped
430 once the gas has cooled down:

$$[\text{H}](t, \vec{r}) = [\text{H}]_0 \psi_0(\vec{r}) \exp\left(-\frac{t}{\tau_0}\right). \quad (7)$$

The function $\psi_0(\vec{r})$ depends on the geometry of the plasma chamber and on the boundary conditions (i.e. on the loss probability at the wall) and can be easily determined for simple geometries. As mentioned previously, the plasma region in the present experiment has a simple cylindrical geometry. The characteristic time of the first order mode depends on the loss probability at the wall [23] and can be approximated by:

$$\tau_0 = \frac{\Lambda_0^2}{D} + \frac{V}{A} \cdot \frac{2(2 - \gamma_s)}{\gamma_s \langle v \rangle}, \quad (8)$$

where A is the area of the wall surface, V is the chamber volume, $\langle v \rangle$ is the H atom thermal velocity, γ_s is the surface loss probability and Λ_0 is the diffusion length determined by the reactor geometry and dimensions.

The H atom density decrease obtained experimentally was fitted by an exponential function and the characteristic time obtained were used to determine the loss probability at the wall from Eq. 8. Let us note that this approach gives an average loss probability on all surfaces in contact with the plasma. Since all surfaces in contact with plasma are quartz surfaces in the present study, it allowed us determining atomic loss probability on quartz.

Eq. 8 is valid only if the diffusion coefficient is constant in time and space. However, under our experimental conditions the gas was quite hot during the plasma pulse [5] and the diffusion coefficient was varying with time in the post discharge due to gas cooling. For this reason, as previously stated, data acquired at time shorter than one millisecond were disregarded for the determination of surface loss probability. The diffusion coefficient was calculated as follows:

$$D = \frac{\pi}{8} \lambda \langle v \rangle, \quad (9)$$

with the mean free path $\lambda = \frac{1}{\sigma N}$, N being the neutral gas density and $\sigma = 2.2 \cdot 10^{-19} \text{ m}^2$ the momentum transfer cross section given by Krstic and Schultz [24]. They demonstrated that the cross section is identical for hydrogen, deuterium and tritium whatever the collision partners (H with H_2 , H with HD, D with D_2 , etc).

Exponential fits of atomic decays are presented on Figure 5, Figure 8 and Figure 9. The corresponding decay times are given in Table II together with the deduced loss probability for both hydrogen and deuterium (from Eq. 8). The obtained loss probabilities are for atoms

460 at ~ 300 K interacting with a quartz surface at ~ 300 K. In his article [23] Chantry evaluated
 461 the error made by using the approximate analytical solution (Eq. 8) to determine decay time,
 462 as a function of container aspect ratio and surface loss value. The error made under our
 463 experimental conditions can be estimated thanks to Figure 4 of reference [23] (cylinder with
 464 an aspect ratio of 2, diffusion of H atoms with a loss probability at the wall of $\sim 2\%$) and
 465 leads to an overestimation of the loss probability by 6% at maximum. The loss probabilities
 466 presented in Table II have been corrected accordingly.

TABLE II. Decay time constants for H and D obtained by exponential fit of the experiments and the corresponding surface loss probabilities

| | τ_{H} (ms) | τ_{D} (ms) | γ_{Hcorr} | γ_{Dcorr} |
|----------------------------------------------|------------------------|------------------------|-------------------------|-------------------------|
| Pure gas 10 Hz | 2.48 ± 0.08 | 3.90 ± 0.22 | 0.019 ± 0.001 | 0.017 ± 0.001 |
| H ₂ :D ₂ mixture 10 Hz | 2.89 ± 0.17 | 3.77 ± 0.23 | 0.016 ± 0.001 | 0.018 ± 0.001 |
| Pure gas 1 Hz | 2.46 ± 0.11 | - | 0.019 ± 0.001 | - |

467 C. Discussion

468 1. Atomic surface loss

469 As discussed in the introduction, many measurements of hydrogen surface loss probab-
 470 ities on various surfaces can be found in the literature but only a part of them deal with
 471 glass surfaces [25–31], and to the best of our knowledge none of them consider deuterium
 472 atoms. Furthermore, for any kind of material, results are generally scarce and can span over
 473 two or three orders of magnitude [27]. This is because atomic surface loss strongly depends
 474 on surface state [32] which is not controlled under plasma exposure. Surface state depends
 475 on surface temperature, positive ion flux, positive ion energy, atomic flux, base pressure,
 476 gas purity, etc. Most of these parameters depend on experimental conditions (pressure,
 477 power, etc). Furthermore atomic surface loss might also depends on plasma parameters
 478 such as the atomic temperature in the vicinity of the wall as demonstrated recently [22].
 479 As a consequence, comparisons between different plasma reactors, with different pressure
 480 or power conditions are rather difficult to perform. However, there are few general trends
 481 that can be extracted from the literature. First, surface loss probabilities are usually higher

482 when surfaces are directly exposed to the plasma (measurement in the discharges or in the
483 post discharges) than when they are not (measurement in flowing afterglow) [33]. This is
484 probably due to the very different surface states obtained when surfaces are exposed to
485 positive ion bombardment which are thought to have a cleaning effect. Adsorbed water
486 molecules that poison atomic recombination at surfaces are for instance probably desorbed
487 due to ion bombardment [34]. H surface loss probabilities on glass surfaces ranging from
488 10^{-5} to $8 \cdot 10^{-2}$ can be found in the literature [27]. If measurements in spatial afterglow
489 are excluded, measurements still range between $\sim 10^{-4}$ and $\sim 10^{-2}$ [26, 27]. Some pressure
490 resolved studies [35–39] seem to indicate that H atom loss probabilities on aluminium and
491 stainless steel are higher in low-pressure high density plasma sources, such as the one used
492 in the present study, than in higher pressure sources. This has been summarised by Sode et
493 al [40]. Booth et al have shown for oxygen atoms loss on Pyrex that two pressure regimes
494 might exist [22]. A high pressure regime (above 100 Pa in their experimental device) where
495 atomic loss probability variations are fully explained by the atomic temperature close to the
496 wall, and a low pressure regime with an increase of loss probability that cannot be explained
497 by the atomic temperature. This increase might be due to an increasing influence of positive
498 ion bombardment on the walls due to a decrease of sheath collisionality at lower pressure. In
499 this study, measurements were limited to a minimum pressure of about 27 Pa. However, it
500 shows that for a proper comparison with existing data, it is preferable to select similar pres-
501 sure ranges and, more generally speaking, similar experimental conditions. In that sense,
502 measurements of H atomic loss on Pyrex done by Samuelli et al [27, 31] are the closest to the
503 present ones. They found a value of $8 \cdot 10^{-2}$ at about 10 Pa and 800 W RF power in a high
504 density helicon plasma source. Even if the pressure and the power density were different in
505 both studies, positive ion flux and positive ion energy were of the same order of magnitude,
506 giving relevance to the comparison. Both measurements give surface loss probabilities much
507 higher than measurements done at higher pressure or in flowing conditions, confirming that
508 in low-pressure high density hydrogen plasmas the atomic loss probability on glass is rather
509 high.

511 It can be noticed from Figure 5, Figure 8, and Figure 9 that deuterium atomic decay time
 512 is noticeably higher than the hydrogen one. However, Table II shows that atomic surface
 513 loss probabilities are similar for both isotopes, both in pure gas and H:D mixture. This
 514 demonstrates that there is no isotopic effect with regards to the atomic surface kinetics, but
 515 there is an isotopic effect on atomic loss. The faster decay time (which means higher loss
 516 rate) of hydrogen atoms is explained by its lower mass giving faster diffusion towards the
 517 wall (first term in Eq. 8) and higher flux to the wall (thermal velocity in the second term).
 518 The latter contribution is the most important, the former contributing only to $\sim 15\%$ to the
 519 decay time.

520 Despite identical surface loss probabilities, the lower loss rate should lead to higher atom
 521 density in D_2 plasmas compared to equivalent H_2 plasmas if the production mechanisms
 522 were identical. In $H_2:D_2$ (50%-50%) plasma it has been observed on the contrary that H
 523 TALIF signal was slightly higher or equal to D one (H to D TALIF ratios were between 1 and
 524 1.3). Two photon absorption cross sections differences between hydrogen and deuterium are
 525 insignificant and can be disregarded [41] for data analysis. Therefore, it is worth discussing
 526 isotope effects on atom production mechanisms in the context of the present paper. Three
 527 production mechanisms are considered and their isotopic effects are discussed: i) electron
 528 impact dissociation of molecules is expected to be the predominant mechanism for atomic
 529 production and therefore must be considered with attention, ii) electron attachment on
 530 vibrationally excited molecules producing a negative ion and an atom is not expected a
 531 priori to be a major source of atomic species but is known to demonstrate a strong isotopic
 532 effect, iii) finally, production of atomic species through positive ion loss is also considered
 533 as it might be of importance in a high density plasma source.

534 Dissociation by electron impact is first considered. Due to the complexity of the disso-
 535 ciation process, there are only a few available data for hydrogen dissociation cross sections
 536 and even fewer for deuterium [42, 43]. H_2 and D_2 dissociation at low electron energy (be-
 537 low ~ 15 eV) proceeds only through the excitation of the pre-dissociative $b^3\Sigma_u$ state. All
 538 references report a maximum cross section for this process at energy in the range 12-18 eV,
 539 with a value between 0.3 and $0.8 \cdot 10^{16}$ cm² [44–49], and close to $0.5 \cdot 10^{16}$ cm² for the most
 540 recent references [47–49]. At energy above the maximum of H_2 ($b^3\Sigma_u$ state) excitation cross

541 section, contributions from other excited electronic states arise and, depending on the refer-
542 ences, dominate [42] or significantly participate [46] to the H₂ total dissociation cross section.
543 There is no measurement of this contribution for D₂. Recent calculations [44, 46] consider
544 the excitation of b³Σ_u state (and therefore the dissociation of the molecule) for H₂ and D₂
545 from threshold to hundreds of eV. At high energy H₂ and D₂ dissociation cross sections are
546 found to be identical while, at energy between threshold and 12 eV, the H₂ cross section is
547 higher by a factor varying from 1 to 10. These results are in contradiction with Celiberto
548 et al [49] who found higher cross section for D₂ at high energy, and in contradiction with
549 Trevisan and Tennyson [48] who found a cross section about two times higher for D₂ at low
550 energy (below 12 eV) [43, 48]. The disagreement at high energy between different studies
551 does not matter too much since in a low electron temperature plasma source, and for a
552 process with a maximum cross section below 20 eV, the contribution of high energy electron
553 to dissociation can be neglected. However, the differences at low energy have a strong effect
554 on the calculation of the dissociation rate.

555 We have calculated the dissociation rate coefficients of H₂ and D₂ for a Maxwellian
556 electron distribution using the most recent cross sections of Refs. [44, 46]. They are
557 plotted as a function of the electron temperature T_e in Figure 10 [50]. Without the quartz
558 tube (stainless steel chamber) and in DC mode, we measured a low electron temperature of
559 0.8 eV at 10 Pa and 1000 W, 5 cm above the wafer [51]. A measurement was also performed
560 with a Pyrex tube equipped with a large enough hole to allow Langmuir probe introduction
561 in the plasma, and an almost similar electron temperature of 0.7 eV [10] was found. However,
562 due to the relatively high pressure considered in the present study, the electron temperature
563 might not be uniform in the plasma. Axial measurements of electron temperature have been
564 performed at 10 Pa and 1000 W in H₂ in another cylindrical plasma reactor equipped with
565 a similar 3 turns RF antenna. The main differences were the chamber radius (10 cm versus
566 8 cm) and the walls made of stainless steel instead of quartz. While the different surface
567 over volume ratio is not affecting too much the electron temperature (as predicted by simple
568 global plasma modelling [52, 53]), the difference in chamber walls might lead to different
569 plasma composition because of the different surface losses and therefore different electron
570 temperature. Thus, the most interesting information is the observed vertical gradient rather
571 than the absolute electron temperature values. The electron temperature has been found to
572 increase from 0.8 eV to 1.45 eV at 5 cm from bottom and 2.45 eV at 10 cm from bottom. An

573 extrapolation of the measurement to 14 cm gives an axially averaged electron temperature
574 at 10 Pa equal to 2.4 eV well above the 0.8 eV measured at bottom and still well above
575 measurement at 5 cm from the bottom. It appears therefore that a spatial distribution of
576 T_e in the plasma reactor has to be considered to study H/D production mechanisms. A
577 simple volume averaged analysis equalling hydrogen production and loss rate tells that a
578 production rate as high as $10^{23} \text{ m}^{-3}\text{s}^{-1}$ is required to account for a H density of $3 \cdot 10^{20} \text{ m}^{-3}$
579 (Figure 4) with H loss frequency of $\sim 350 \text{ s}^{-1}$ ($1/\tau_{\text{H}}$, Table II). Figure 10 presents dissociation
580 production rates ($k_{\text{diss}} n_e [\text{H}_2]$) computed using an electron density of $1 \cdot 10^{17} \text{ m}^{-3}$ and a H_2
581 density of $2.4 \cdot 10^{21} \text{ m}^{-3}$ (10 Pa and 300 K). Dissociation production rate reaches $10^{23} \text{ m}^{-3}\text{s}^{-1}$
582 at an electron temperature of 2.5 eV, or 5 eV if ones takes into account a higher average gas
583 temperature (900 K at 10 Pa [5]) and a lower H_2 density.

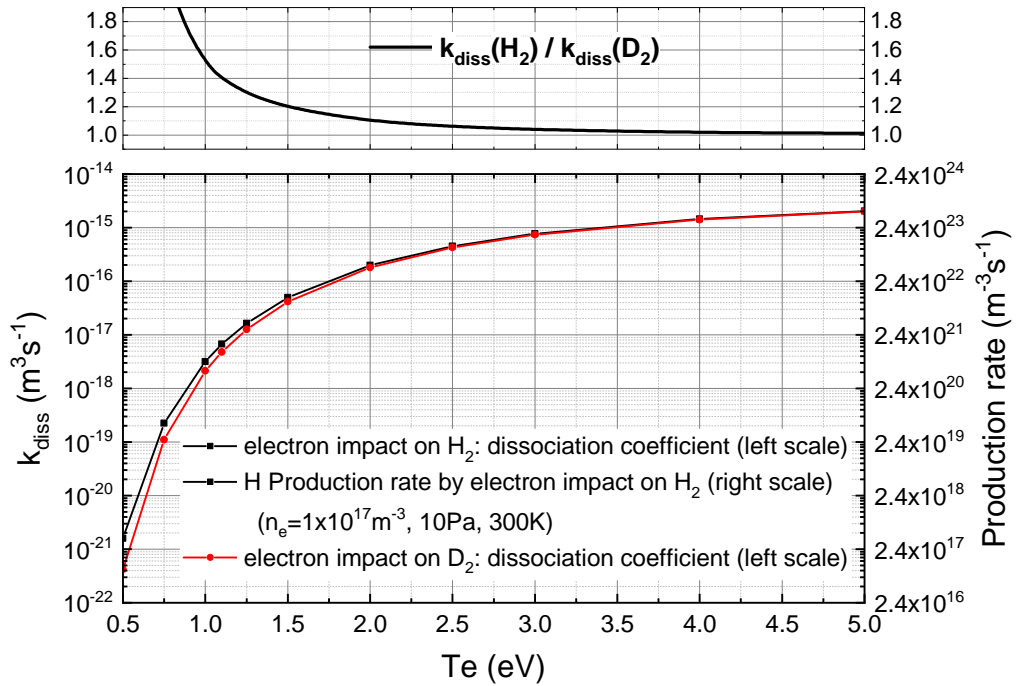


FIG. 10. Electron impact dissociation of H_2 and D_2 as a function of the electron temperature T_e : dissociation coefficients (left scale) calculated for Maxwellian electron distribution functions and H production rate (right scale) given for an electron density of $1 \cdot 10^{17} \text{ m}^{-3}$ and a H_2 density of $2.4 \cdot 10^{21} \text{ m}^{-3}$ (10 Pa and 300 K). On top is given the ratio between H_2 and D_2 dissociation coefficients

584 In order to get a higher or equivalent H density (compare with D one) while H loss rate
 585 is larger by a factor of about 1.3, a dissociation coefficient larger by at least a factor of
 586 1.3 for hydrogen is required. From Figure 10 this can only occur for electron temperature
 587 below 1-1.5 eV. At such low temperature the production rate is too low to have a significant
 588 impact on H and D population. Furthermore, as discussed previously the average electron
 589 temperature is probably much higher than 1 eV in the present plasma source. At higher
 590 electron temperature the higher cross sections for H at low energy ([44] and [46]) have
 591 less importance and the dissociation coefficient ratio is approaching unity. Let us note
 592 however, that at 2.5 eV, when the production rate is reaching the expected value under our
 593 experimental conditions, the H dissociation coefficient is still 5% higher than D one. This
 594 account for a small isotopic effect in atom production. Note however that the 5% difference
 595 between the dissociation coefficients probably falls within uncertainties in the knowledge of
 596 the dissociation cross sections. Finally, it worth mentioning that even if the H atom density
 597 is measured in the region of low electron temperature, it is reflecting the global production
 598 mechanisms in the whole plasma source. Indeed, fast diffusion and low surface loss rate tend
 599 to equalize the H density throughout the reactor volume.

600 Dissociative attachment of an electron on a vibrationally excited molecule is now con-
 601 sidered. Dissociative attachment of an electron on a vibrationally excited hydrogen or deu-
 602 terium molecule is producing one negative ion and one atom. It is known to present strong
 603 isotope dependence, the cross sections for hydrogen being higher by orders of magnitude
 604 than those of deuterium [51, 54–56]. Based on cross sections of [49] (slightly lower than
 605 the original cross sections of Ref. [57]) we have calculated dissociative attachment rate for
 606 a vibrational temperature of 3300 K [5], a hydrogen density of $2.4 \cdot 10^{21} \text{ m}^{-3}$ (10 Pa and
 607 300 K), an electron density of $1 \cdot 10^{17} \text{ m}^{-3}$ and rotationless vibration states from $\nu = 0$
 608 to $\nu = 5$. The maximum production rate is $2 \cdot 10^{20} \text{ m}^{-3}\text{s}^{-1}$, far away from the required
 609 production rate.

610 Finally, atomic production through positive ion loss is considered. At 10 Pa the dominant
 611 positive ion is most probably H_3^+ due to very efficient conversion mechanism of H_2^+ by collision
 612 with H_2 : $\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}$. This reaction creates a hydrogen atom. Furthermore, loss
 613 mechanisms of H_3^+ (or D_3^+) ion create from one to three atoms [19]. If we assume for the sake
 614 of simplicity that all H_2^+ ions are converted into H_3^+ then the production rate of H atoms
 615 through this mechanism is given by the ionisation rate of H_2 (multiplied by a factor from 2 to

616 4 to take into account ion loss). With a hydrogen molecular density of $2.4 \cdot 10^{21} \text{ m}^{-3}$ (10 Pa
 617 and 300 K) and an electron density of $1 \cdot 10^{17} \text{ m}^{-3}$, this production rate reaches $10^{22} \text{ m}^{-3}\text{s}^{-1}$ at
 618 $T_e = 3 \text{ eV}$ and $10^{23} \text{ m}^{-3}\text{s}^{-1}$ at $T_e = 5 \text{ eV}$ (cross sections from [58]). Therefore, between 3 and
 619 5 eV this mechanism could contribute in a non-negligible manner to the atomic production.
 620 Isotopic effect in molecule ionisation or in $\text{H}_2^+/\text{D}_2^+$ ion conversion could therefore influence
 621 the balance between H and D atoms in the discharge. Isotopic effect in electron impact
 622 ionization of hydrogen molecules is documented in particular in Ref. [43]. For electrons from
 623 threshold (16 eV) up to 25 eV the deuterium electron impact total ionization cross section
 624 (dissociative and non-dissociative ionisation) is slightly higher than the hydrogen one (by a
 625 maximum factor of 1.15) and cannot be at the origin of a higher H density. Above 25 eV
 626 there is no more isotope dependence. Concerning isotopic effect in $\text{H}_2^+/\text{D}_2^+$ ion conversion
 627 into $\text{H}_3^+/\text{D}_3^+$ we are not aware of any publication and cannot conclude. Let us note that ion
 628 conversion could contribute by few percent or few tens of percents to atomic production,
 629 and therefore would most probably do not have any major isotopic effect. This point could
 630 only be verified with the development of a dedicated model.

631 This simple analysis shows that for electron temperature around 2-3 eV, which is the
 632 average value expected in the present conditions, there is no obvious isotopic effect in H
 633 and D production mechanisms. On the contrary we have measured a clear isotopic effect
 634 in atomic loss which should lead to higher D than H densities which was not observed. A
 635 complete model, preferentially including vibrational states, would be required to discuss in
 636 details the isotopic effects and to explain these experimental observations. Besides, more
 637 experiments would be necessary to validate the set of cross sections to be used. Dissociation
 638 cross sections could be investigated for instance by using the positive column of a higher
 639 pressure DC discharge where the electron temperature is homogeneous and in the appro-
 640 priate range ($\sim 2 \text{ eV}$), such as it has been carefully done recently for the dissociation cross
 641 sections of CO_2 [59].

642 An important outcome of the present work is that the same surface loss probability was
 643 measured for H and D on quartz. Lamara et al [17], and other authors previously [60, 61],
 644 found H and D densities in plasmas corresponding to the $\text{H}_2:\text{D}_2$ mixture ratio. Lamara et
 645 al suggested that D surface loss probability was higher than the H one, but their suggestion
 646 was based on Trevisan and Tennyson [48] dissociation cross sections demonstrating higher
 647 values for D_2 than H_2 . However, not all dissociation cross section sets are demonstrating

648 such effect and our work is showing that deuterium surface loss probability is not higher than
649 the H one. Galante et al [62] suggested that the higher atomic density they measured in D₂
650 helicon plasmas with respect to H₂ plasmas was due to the mass difference (and therefore to
651 a slower diffusion and a lower flux to the wall). This is consistent with the results obtained
652 here showing smaller D decay time.

653 **IV. CONCLUSION**

654 In this paper we have measured hydrogen and deuterium atomic loss probabilities on
655 quartz in low pressure high density inductively coupled plasma source. The surface loss
656 probability found for H is much higher than the value found at higher pressure in good
657 agreement with recent measurements in similar experimental conditions [27, 31]. In pure
658 hydrogen/deuterium gas or in mixture gas, no isotopic effect on surface kinetics has been
659 observed and the surface loss probability of H and D were found to be almost identical and
660 equal to ~ 0.018 (1.8%). However, despite the lack of difference in surface loss probability,
661 there is a net isotopic effect on surface loss rate due to the difference in mass between the
662 isotopes leading to higher diffusion to the wall and higher flux at the wall for hydrogen
663 atoms (the hydrogen atoms are lost faster than the deuterium ones).

664 Based on this isotopic difference and on the comparison between H and D TALIF signals,
665 we discussed the atomic production mechanism isotopic effects. Three production mecha-
666 nisms were considered, namely dissociation of the molecule by electron impact, dissociation
667 by electron attachment, and ion conversion. Based on existing cross sections and on simple
668 volume averaged analysis, no clear isotopic effect could be demonstrated for an electron
669 temperature range relevant for the present study. In our case, a clear isotopic effect in atom
670 loss was measured but with almost equivalent H and D atom density. Thus, a definite
671 conclusion would require further analyses and vibrational state resolved modelling for both
672 hydrogen and deuterium.

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