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# Isotope effect in plasmas driven by ECR modules towards $H^-$ and $D^-$ production

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## Abstract

Optimization of negative ion sources operated with deuterium may be limited by the lack of data on fundamental processes. Insight can be obtained from studies focusing on a direct comparison of  $H_2$  and  $D_2$  plasmas. Herein, the ECR volume negative ion source "Prometheus I" operates with both  $H_2$  and  $D_2$  gases and the properties of the generated plasmas are probed by means of electrostatic probe and laser induced photo-detachment. A parametric study, involving pressure and microwave (2.45 GHz) power variation, reveals similar qualitative trends for most of the plasma properties in both gases. However, quantitatively, differences do exist for the plasma potential, the electron density and temperature, and the negative ion to electron density ratio. EEDFs are thus isotope dependent. Overall, nearly the same maximal  $H^-$  and  $D^-$  negative ion densities are achieved (i.e.,  $4 \times 10^9 \text{ cm}^{-3}$ ). The results are eventually elucidated with respect to the ECR heating mechanism, and the production and destruction paths of the negative ions.

**Keywords.** ECR plasmas; Negative ions; Hydrogen; Deuterium; Photo-detachment; Probes.

## I. Introduction

The heating and current drive of the plasma in ITER will rely on the injection of a total of 33 MW of 1 MeV  $D^0$  [1,2]. The formation of these powerful  $D^0$  beams will be based on the neutralization of accelerated  $D^-$  beams since, at such high energies, the efficiency of this process remains acceptable (~56%) for negative ions but becomes unsuitably low for positive ions [2,3]. ITER's neutral beam cell will be equipped with four injectors: three heating neutral beams (the third will be employed in the event of a future upgrade to 50 MW of injected power), and a diagnostic neutral beam [4]. The most critical component of a heating neutral beam is the negative ion source itself, expected to provide either a 1 MeV  $D^-$  beam or a 0.87 MeV  $H^-$  beam of an accelerated current density of 200 A  $m^{-2}$  or 260 A  $m^{-2}$  and an accelerated current of 40 A or 46 A, for a duration of 3600 s or 1000 s, respectively, operating in both cases at a filling pressure of 0.3 Pa or less [1,2,4]. Operation with hydrogen is foreseen for the early, non-nuclear phases of ITER [2].

The only types of negative ion sources that have been deemed capable of meeting these requirements are the ones driven by Cs/arc or radio frequencies (RFs) [1]. However, an RF source was finally chosen to be utilized in ITER's injectors since it is free of filaments and thus there is no need for regular maintenance. This is in line with the concept for full remote handling during ITER's active phase [1,4]. ITER's source design follows a modular concept based on eight RF drivers, with each driver being based on the RF prototype source "BATMAN" [5-8]. In this type of source, negative ions are formed mainly through the surface production process [8,9].

The half-ITER-size ion source "ELISE" is an intermediate step towards the ITER neutral beam injector source that has been dedicated to resolve issues of technical or physical nature that inhibit the fulfillment of the ITER requirements [10,11]. Knowledge gained from "ELISE" is exploited by "SPIDER", a full-scale injector source. Though only able to provide a 100 keV neutral beam, research focuses on further optimization of the source performance, e.g., in terms of source uniformity over a beam area of about 1.5  $m^2$ , negative ion current density, beam optics, beam source operation for 3600 s, and Cs distribution [12]. Eventually the second test bed, "MITICA", a complete full-scale injector embodying all ITER specifications, is foreseen to exhibit the overall target performance [12].

Up to date, "ELISE" has successfully demonstrated  $H^-$  pulses of 1000 s with a current density corresponding to 90% of the ITER goal [12]. On the other hand, the transition to deuterium has proven to be far more challenging as various complications stem from the inherent isotopic differences between hydrogen and deuterium. Some important issues are the generally higher, inhomogeneous, and less stable co-extracted electron current, the significantly larger amount of Cs needed for stabilizing this current, and the Cs depletion from the source walls and the plasma grid due to the higher atomic mass of deuterium [10,11]. Although considerable progress has been made after the application of refined Cs evaporation and distribution procedures, and though ITER requirements have nearly been reached for short  $D^-$  pulses, still only 66% of the ITER demand for negative ion current density can be extracted, over a time span of 45 min [10,11].

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2 In line with the above brief presentation, it becomes apparent that any lab-scale fundamental study on a  
3 direct comparison between  $H_2$  and  $D_2$  plasma properties would be of added value. Indeed, this task has triggered  
4 the interest of different research groups, regardless of the type of the source employed. Namely:

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6 As regards filament-driven sources, Cs-free discharges of both gases have been examined in the sources  
7 “Camembert II” and “Camembert III” [13,14]. The results indicate, briefly: (i) the electron density is consistently  
8 higher in  $D_2$  with respect to  $H_2$ , in both sources; (ii) the electron temperature shows no significant change between  
9  $H_2$  and  $D_2$  discharges in the larger source, as opposed to the smaller source in which it is lower in the case of  $H_2$ ;  
10 (iii) the negative ion density and negative ion to electron density ratio is generally lower in  $D_2$  than in  $H_2$  in both  
11 sources, nevertheless these two parameters attain greater absolute values in the smaller source [14]. Observations  
12 (i) and (ii) have also been reported in the “Culham” source [15,16]. Additionally, in this latter source, a higher plasma  
13 potential has been measured in  $D_2$  while the fast electron density and temperature remain the same in both  $H_2$   
14 and  $D_2$ . In another work in “Camembert II”, two-laser photo-detachment has been used to infer the  $H^-$  and  $D^-$  ion  
15 temperatures, with the latter being lower [17]. Pure volume production of  $H^-/D^-$  in a rectangular arc chamber, with  
16 an external pair of permanent magnets in front of the plasma grid serving as a magnetic filter, has been the subject  
17 of other works [18,19]. Spatially resolved measurements with simultaneous variation of the magnetic filter field  
18 intensity revealed that the values for electron density and temperature were slightly higher in  $D_2$  than in  $H_2$ .  
19 Furthermore, a stronger magnetic filter field is required to control the electron temperature in the  $D_2$  plasma. In  
20 other filament-driven sources the isotope scaling has been investigated based on measurements of the extracted  
21 beam properties [20,21], along with probing of the characteristics of the plasma created in the vicinity of the  
22 extraction region [22,23]; the bottom line in the findings is that the extracted  $D^-$  ion current is constantly lower,  
23 accompanied by a larger co-extracted electron current. Moreover, the enhancing effects of Cs seeding on both  $H_2$   
24 and  $D_2$  plasma properties, as opposed to Cs-free discharges, has been highlighted in studies at the “Camembert  
25 III” [24], “MANTIS” [25], and elsewhere [26]. In the filament driven “LIISA” ion source used at the “JYFL K130”  
26 cyclotron, the VUV emission spectra for both  $H_2$  and  $D_2$  have been compared. Neither the spectra nor the  
27 volumetric rates of ionization, excitation, production of high vibrational states, and dissociation between the two  
28 isotopes showed any significant difference. It is therefore suggested that in this source, the observed difference  
29 between the  $H^-$  and  $D^-$  production through dissociative electron attachment (DEA) is attributed most likely to the  
30 difference in the diffusion properties of hydrogen and deuterium [27].

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32 As for inductively coupled plasma setups other than the prototypes described at the beginning of the  
33 present section, work [28] deals with the cases of  $H_2$  and  $D_2$  and shows that the atomic density is higher in  $D_2$ .  
34 Furthermore, atoms were found to be more efficiently ionized than the respective molecules, leading thus to a  
35 significantly elevated electron density in  $D_2$  compared to  $H_2$  and, consecutively, to a higher RF power transfer  
36 efficiency. Another setup, named “ACCesS”, has been employed in experiments relevant to surface production of  
37 negative ions [29]. It was concluded that, no significant isotope effect occurs regarding the surface negative ion  
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1 formation. The reader is also referred to reports [30,31] for further studies concerning a comparison between  
2 surface production of  $H^-$  and  $D^-$ .  
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5  $H_2$  and  $D_2$  discharges in RF-driven sources of a different type, i.e., helicons, have been studied in reference  
6 [32] as well as at the “RAID” source [33,34]. In [32] the density ratio of atomic to molecular deuterium was found to  
7 be higher than the respective ratio for hydrogen. In [33] the degree of dissociation and the ion densities were higher  
8 for deuterium than for hydrogen. In [34], the electron density was higher in the case of  $D_2$ , the electron temperature  
9 appeared to be nearly the same for  $H_2$  and  $D_2$ , and the negative ion density and the negative ion to electron density  
10 ratio was lower in  $D_2$ .  
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15 Additionally, an electron cyclotron resonance (ECR) source with driven plasma rings has been studied in  
16 terms of extracted  $H^-$  and  $D^-$  ion current as a function of the pressure, the power, and the immersion depth of the  
17 plasma electrode into the plasma volume [35]. The  $D^-$  current was found to be less. Dissociative attachment of  
18 electrons to molecules at high Rydberg excited states was identified as the most probable process for  $H^-$  and  $D^-$   
19 formation. Another ECR source, but of a tandem configuration, named “HOMER”, has been studied for the case of  
20  $H_2$  [37,38]. In this source, the efficiency of materials with a low work function on the surface production of negative  
21 ions has also been investigated [39,40]. Particularly for the material MoLa,  $D_2$  was also tested and while varying  
22 the isotope had an influence on the plasma parameters, the resulting effects on the negative ion formation  
23 compensated each other leading to comparable negative ion densities [39].  
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31 On the other hand, there is an alternative concept for ECR heating of  $H_2$  and  $D_2$  plasmas, based on the  
32 use of elementary dipolar ECR modules [41]. Negative ion sources reporting the use of this kind of ECR modules  
33 are “Camembert III” [42-46], “ROSAE III” [46,48], “SCHEME” [49,50], and “Prometheus I” [47,51-53]. “Camembert  
34 III” and “ROSAE III” have been operated and characterized in hydrogen only. “SCHEME”, however, has been  
35 employed in experimental campaigns (i.e., synchrotron-based VUV absorption spectroscopy) involving both  $H_2$   
36 [49] and  $D_2$  [50]. In summary, **Table I** provides the available data for the ECR sources of different configurations,  
37 including the data quoted by the present study.  
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43 Hereby, in the ECR volume source “Prometheus I”, the research of the hydrogen plasma [47,50-53] is  
44 extended to deuterium. Basic plasma properties are accessed via probe measurements and laser-induced photo-  
45 detachment. The experiments are realized throughout the available range of the injected microwave (MW) power  
46 and the working pressure. The results are then compared and evaluated to identify similarities and differences  
47 between the ECR plasmas of the two isotopes. The isotope effect is mirrored on the electron energy distribution  
48 functions (EEDFs) of the  $H_2$  and  $D_2$  plasmas, and it is also noticeable on the negative ion to electron density ratio.  
49 Despite that, comparable  $H^-$  and  $D^-$  negative ion densities are achieved, and this apparent discrepancy is evaluated  
50 on a theoretical base.  
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## II. Experimental setup

A conceptual design of the experimental setup is illustrated in [Fig. 1](#). A thorough description of the negative ion source Prometheus I is given in [\[51-53\]](#). Briefly, it consists of a  $240 \times 240 \times 240 \text{ mm}^3$  (inner dimensions) stainless steel chamber with viewports for the installation of plasma diagnostics. The source is evacuated to a base pressure of around  $5.33 \times 10^{-5} \text{ Pa}$  by a turbomolecular pump (Adixen ATP 80) backed up by a rotary pump (Adixen PASCAL 2021 SD). Operation within the pressure range of 0.13 – 2.67 Pa (measured by a MKS Baratron® 627D capacitance manometer) may be achieved by the insertion of either  $\text{H}_2$  (99.999%; AirLiquide) or  $\text{D}_2$  (99.8%; Linde) gas by means of a digital mass flow controller (MKS 1179B). Three representative pressures are here studied (0.53, 1.07 and 1.60 Pa; fixed when plasma ON). The plasma is sustained by an array of five elementary ECR modules [\[41\]](#) driven by independent solid-state microwave generators (SAIREM; 2.45 GHz), each capable of delivering a maximum power of 180 W. Herein, the injected power is varied from 30 to 180 W per module (0.15 to 0.9 kW in total).

Source wall conditioning requires special attention since, a notable difference in the plasma properties is observed when the two gases are interchanged. This effect can most likely be attributed to the adsorption of remainders of the formerly used gas into the interior surfaces of the source, also known as gas retention [\[54\]](#). To ensure wall recovery, i.e., eliminate this issue and achieve stable and reproducible plasma properties, various trials led to the following protocol: each gas switch is followed by a bake-out of the source at  $150^\circ\text{C}$ , under base pressure conditions, for at least 30 h.

Throughout the experimental series, the temperature of the source walls is not controlled in any manner, therefore it is solely influenced by the operational parameters and the measurement sequence. However, it is monitored using a thermocouple for consistency reasons. In between measurements, a 20-min interval is allowed for the thermal stabilization of the source. [Table II](#) provides collective information on the experimental conditions for each value of the working pressure and for the minimum and maximum power settings.

The produced plasma is characterized by means of Langmuir probe and laser photo-detachment ([Fig. 1](#)). The probed area corresponds to the center of the source and at a 65 mm distance downstream of the midplane of the magnet of the central ECR module. The probe is made of a 0.25 mm in diameter tungsten wire and the tip (exposed to the plasma) is L-bent such that to be coaxially aligned with the laser beam for the photo-detachment measurements. The tip length is 15 mm in total with the bent part being 11 mm. The rest of the wire is housed in a telescopic configuration of dielectrics (an alumina tube inside a wider quartz tube) to insulate and protect it from the plasma. Part of the quartz tube is supported inside a stainless-steel tube that ends in a standard BNC vacuum feedthrough. A CF flange-to-quick connect coupling adapter makes a vacuum sealing with the steel tube and at the same time allows the linear translation of the probe [\[53\]](#). I–V characteristic curves are acquired by a lab-made, automated system of high accuracy [\[55\]](#). The probe voltage is swept from -70 V to 30 V with a step of 97.6563 mV. At each voltage step  $2^{12}$  samples are averaged with a routine embedded in the system microcontroller, to increase

the signal-to-noise ratio. Prior to each acquisition, the tip surface is cleaned by heating induced by a high electron current, over 10 s which is then followed by another 10 s of cooling.

The processing of the I–V curves in order to gain access to main plasma parameters (i.e., plasma potential  $V_p$ , floating potential  $V_f$ , cold electron density  $n_{e(cold)}$ , and hot electron density  $n_{e(hot)}$ ) has been described previously [53]. Briefly, the floating potential is defined as the potential for which the current collected by the probe equals zero, while the plasma potential is determined from the maximum of the first derivative of the I–V curve. The positive ion current is extrapolated linearly from the data at high retarding potentials and subsequently subtracted from the I–V curve. The remaining current, i.e., the electron current, is fitted as the sum of two exponentials, following iterative methods; residuals lower than 10% are achieved (Figs. A1 and A2; Appendix). This points to a bi-Maxwellian electron energy distribution function (EEDF), implying two electron populations (hereafter “cold” and “hot” electrons). The density and temperature (quoted in eV) of the two populations, i.e.,  $n_{e(cold)}$ ,  $n_{e(hot)}$  and  $kT_{e(cold)}$ ,  $kT_{e(hot)}$ , respectively, are extracted from the fitting parameters of each exponential. Apart from the two exponentials, EEDFs are also constructed by using the Druyvesteyn method.

The components for the laser induced photo-detachment assembly are presented in Fig. 1. The laser employed (Nd:YAG; Quantel Brilliant EaZy) has the following specifications: 1064 nm (1.2 eV) photon wavelength (energy), 3 mm output beam radius, 330 mJ max energy per pulse, 10 ns pulse width, and 10 Hz repetition rate. The beam energy is precisely adjusted either by varying the delay between the laser flash lamp and the Q-switch or by the in-line installation of a half wave plate mounted on a precision rotational stage followed by a thin film polarizing beam splitter. This concept is based on Malus law and allows for the attenuation of the linearly polarized laser beam as a function of the angle between the beam’s initial direction of polarization and the axis of the polarizer. Fig. A3(a) shows the corresponding calculated and measured attenuation curves.

Special attention is paid for the proper application of the photo-detachment technique [56]. Accordingly: (i) the beam radius set here, i.e., 2.5 mm, is larger than the probe collection radius (typical 0.1 mm under the present conditions). (ii) The beam energy density, i.e., 70 mJ cm<sup>-2</sup> inside the vacuum chamber after considering an ~7% attenuation due to the glass viewport (Fig. A3(a)), suffices to detach the excess electron from all the negative ions within the irradiated volume. (iii) The probe bias voltage, i.e., +15 V, is adequate to collect all the photo-detached electrons around it. The impulse of the photo-detached electrons is recorded with a wideband current transformer (Pearson Electronics Inc.; Model 6585; 400 Hz - 250 MHz) on a digital oscilloscope (LeCroyWaveSurfer 104Xs-A; 1 GHz; 5 GSamples s<sup>-1</sup>), without the use of a conventional decoupling circuit [57].

Regarding the laser beam energy density and the probe bias voltage, the above-mentioned values are justified by tests as those shown in Figs. A3(b) and A3(c). In Fig. A3(b), the theoretical relation [56] of the fraction of the detached ions as a function of the beam energy density is reproduced experimentally at typical operating conditions. The saturation of this fraction is predicted and also measured at energy densities as low as ~25 mJ cm<sup>-2</sup>. In Fig. A3(c) the ratio between the peak of the photo-detached electron transient impulse and the steady state electron current versus an increasing probe bias voltage is presented. A positive probe bias of 15 V leads to

1 a quasi-saturation of this ratio. The plasma potential in D<sub>2</sub> is permanently higher than in H<sub>2</sub> (Fig. A4; Appendix)  
2 and the bias of 15 V is 1.5-3 times higher than any plasma potential measured, independently of the gas, pressure,  
3 and power. This value is also selected as a compromise between acceptable saturated ratio and prevention of the  
4 probe tip incandescence which takes place at higher bias voltages.  
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### 10 III. Results

11 In this section the main experimental results are categorized, compared, and primarily commented. A detailed  
12 discussion and physical interpretation of those is carried out in the next section; IV. Discussion. For now, as it has  
13 already been mentioned, we underline the production of two electron populations of different energies (“cold” and  
14 “hot”) due to the heating induced by the present ECR design [58].  
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18 **Fig. 2** gives the evolution of the cold electron density versus the MW power in both H<sub>2</sub> and D<sub>2</sub> plasmas,  
19 with the working pressure as a parameter. The order of magnitude of the density is between 10<sup>10</sup> and 10<sup>11</sup> cm<sup>-3</sup>,  
20 while D<sub>2</sub> plasma is associated with higher cold electron densities independently of the pressure and the power  
21 level. In general, higher power or pressure leads to increased cold electron densities.  
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25 **Fig. 3** presents the corresponding to **Fig. 2** results for the density of the hot electrons. It is reminded that  
26 the present study deals with the negative ion production region, i.e., the region downstream of the ECR driving  
27 region, and thus the hot electron population is not probed in its totality (see further discussion in Section IV). The  
28 absolute density was found to be about 2 orders of magnitude lower than that of the cold electrons. Furthermore,  
29 higher power or pressure leads to increased hot electron densities, similar to the cold electron case. On the other  
30 hand, the isotope effect seems to be less pronounced in the case of the hot population, since its density in the H<sub>2</sub>  
31 and D<sub>2</sub> plasmas tends to deviate less (compare **Figs. 2** and **3**).  
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38 The representative results of **Figs. A1** and **A2** in the Appendix, as well as previous studies [53], have  
39 shown that, the above-mentioned populations follow quasi-Maxwellian distributions. This fact has been confirmed  
40 over all the operational windows studied herein. **Figs. 4** and **5** provide a direct comparison of the EEDFs  
41 established in the H<sub>2</sub> and D<sub>2</sub> plasmas. To the best of our knowledge, a main gap exists in the literature as regards  
42 the study of the isotope effect on the EEDFs. Thus, the present results suggest divergence between the H<sub>2</sub> and D<sub>2</sub>  
43 plasma EEDFs. As it is expected, EEDFs are also pressure and power dependent (only the pressure dependence  
44 is given in **Figs. 4** and **5**). Such differences could regulate production and destruction processes of the H<sup>-</sup> and D<sup>-</sup>  
45 negative ions (see section IV).  
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52 The existence of an isotope effect for the EEDFs, as it is demonstrated in **Figs. 4** and **5**, is further supported  
53 if one considers the pressure and power dependence of the cold and hot electron energies in H<sub>2</sub> and D<sub>2</sub>, and  
54 correlate them with the corresponding densities (**Figs. 2** and **3**). **Fig. 6** displays the existence of higher cold electron  
55 energies in the D<sub>2</sub> plasmas. Otherwise, the ECR heating leads to higher electron energies versus the MW power  
56 in both gases. The temperature of the hot electrons, downstream of the ECR zones, is almost constant (around 15  
57 eV) at any experimental condition (**Fig. 7**) (see further discussion in Section IV).  
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Summarizing, D<sub>2</sub> plasma gives cold electrons of higher density and temperature than H<sub>2</sub> does under identical working conditions. H<sub>2</sub> and D<sub>2</sub> plasmas give, downstream of the ECR zones, hot electrons of comparable temperature whereas their density is either equal (Fig. 3(b)) or slightly higher (Figs. 3(a) and 3(c)) in D<sub>2</sub>, under identical working conditions. These features are reflected on the EEDF curves (Figs. 4 and 5). EEDFs with respect to the negative ion production/destruction are commented later.

Fig. 8 unveils the H<sup>-</sup> and D<sup>-</sup> negative ion density as either the MW power or the gas pressure increases. Higher values of both working parameters lead to higher densities of negative ions. It is worth noticing that the densities achieved are either equal (Fig. 8(b)) or slightly higher (Figs. 8(a) and 8(c)) in H<sub>2</sub>. In any case, values up to about  $0.4 \times 10^{10} \text{ cm}^{-3}$  are reached in both the H<sub>2</sub> and D<sub>2</sub> plasmas.

Despite the close negative ion densities obtained in H<sub>2</sub> and D<sub>2</sub>, the ratio of the negative ion to cold electron density is higher in the H<sub>2</sub> plasmas for any pressure and power level (Fig. 9). This ratio is an important parameter affiliated with the ratio of the negative ion to electron co-extracted currents in ECR-driven sources [44]. Thus, as Fig. 9(b) attests, a ratio of ~0.225 is optimally achieved in H<sub>2</sub> versus ~0.125 in D<sub>2</sub>. Additionally, the data of Fig. 9 disclose that intermediate pressure and power are needed for maximizing this ratio. In Fig. 9, the optima are 1.07 Pa/0.4 kW for H<sub>2</sub> and 1.07 Pa/0.3 kW for D<sub>2</sub>.

The pressure dependence of the negative ion density and the above ratio is better seen in Fig. 10. It is evident that as the pressure increases, a steep negative ion density rise is followed by a quasi-saturation phase; Fig. 10(a). The curves are almost independent of the isotope, in line with the data of Fig. 8. Then, the existence of a distinct optimal pressure to enhance the negative ion to cold electron density ratio is shown; Fig. 10(b). This optimum is located at around 1.33 Pa in both discharges (H<sub>2</sub> and D<sub>2</sub>). As mentioned above (Fig. 9), the H<sub>2</sub> plasma yields a higher value of this ratio.

Finally, a decoupling from the operating parameters and a direct comparison of the negative ion yields in the H<sub>2</sub> and D<sub>2</sub> discharges in terms of endogenous plasma properties, may be attained by plotting the negative ion density versus the plasma density. This is shown in Fig. 11. H<sub>2</sub> plasma allows to produce higher negative ion density than D<sub>2</sub> plasma does for a given cold electron density (Fig. 11(a)). At the same time, the negative ion densities in the two plasmas are neared when the hot electron density is considered (Fig. 11(b)).

#### IV. Discussion

This section outlines the concept of the ECR heating adopted in this work. Then, in light of the present results, it correlates this concept with the EEDFs, and the production and destruction mechanisms of the H<sup>-</sup> and D<sup>-</sup> negative ions. These mechanisms refer to dissociative attachment, and associative detachment and mutual neutralization, respectively.

##### A) ECR heating concept and EEDFs

At the microwave frequency of 2.45 GHz, the magnetic induction required for the ECR condition is  $875 \times 10^{-4} \text{ T}$ . For the ECR modules employed here [41,58], the plasma is produced by electrons accelerated in the region of the

ECR coupling due to the microwave electric field applied via a coaxial line and a permanent magnet at the termination of this line. The trajectories of the electrons in such a multipolar magnetic field have been studied previously [59,60]. In this region, EEDFs appear as the sum of two electron populations. The temperature of the hot electron population can reach more than 17 eV [58]. The plasma is produced by inelastic collisions of these electrons, and it diffuses away from each magnet (see Refs. 1–10 in [41]). Especially for the electrons, in principle hot ones remain trapped in the magnetic field, whereas cold electrons diffuse away from the magnetic field under the influence of density gradients and the resulting space charge electric field [58]. This fact may explain the much lower density (Fig. 3) as well as the almost constant temperature (Fig. 7) of the hot electrons found downstream of the ECR zones, i.e., we probably probe the small fraction of the hot electrons that are capable to escape from the above magnetic filter.

Regarding the isotope effect for the EEDFs shown in Figs. 4 and 5, this may be due both to the different total (i.e., contribution from both dissociative and non-dissociative ionization, in the ECR zones) ionization cross section values for H<sub>2</sub> and D<sub>2</sub>, which give an isotope effect near the threshold electron-impact energies [80]. As predicted theoretically,  $Q_{ion}^{D_2} > Q_{ion}^{H_2}$  up to 25 eV energy but the cross sections at electron energies larger than 25 eV become equal. Indicative values of the total ionization cross section include  $Q_{ion}^{D_2}/Q_{ion}^{H_2} = 1.147$  at 16 eV and  $Q_{ion}^{D_2}/Q_{ion}^{H_2} = 1.041$  at 22 eV [80].

Apart from the differences in the ionization cross sections, the ion confinement time in D<sub>2</sub> is  $\sqrt{2}$  times higher than in H<sub>2</sub> due to the square root of the mass ratio of the two molecules [13,16], while the positive ions are destroyed by transport to the walls where they are neutralized. Thus, the positive ions are consistently higher in D<sub>2</sub>. In other words, the plasma density should be consistently higher in D<sub>2</sub> than in H<sub>2</sub> and their ratio should vary by a factor of about  $\sqrt{2}$ . Fig. 12 provides a direct comparison of this plasma density ratio using the values measured in the present work. The ratio approaches but does not precisely equal  $\sqrt{2}$ , depending on the operating conditions. It indicates that other factors (e.g., the presence of magnetic field, isotope effects in some of the ion-loss cross sections, etc.) may be significant [13,16].

The role of the implied bi-Maxwellian EEDFs in the yield of the H<sup>-</sup> and D<sup>-</sup> ions is clarified by considering their main production and destruction processes.

#### B) Negative ion production reactions and lower energy part of EEDFs

Table III summarizes the main production processes for the H<sup>-</sup> and D<sup>-</sup> negative ions. It is generally accepted that the key path for the volume production is the DEA process (reactions R1 and R2), having cross sections as shown in Figs. 13(a) and 13(b) respectively. In both the H<sub>2</sub> and D<sub>2</sub> plasmas, the cross section highly increases as the vibrational level increases and, simultaneously, the (electron) energy threshold of the reaction shifts to lower values. In our case, a direct comparison between EEDFs and DEA cross sections in Figs. 13(a) and 13(b) shows that the cold populations produced in both the H<sub>2</sub> and D<sub>2</sub> plasmas have energies that promote R1 and R2. On the other hand, the DEA cross section is higher in H<sub>2</sub> than in D<sub>2</sub> for every vibrational level and the energy threshold is lower for the same vibrational level.

**Fig. 13(c)** presents the average  $H^-$  and  $D^-$  ion densities measured within even spaced intervals of electron temperature. This figure is obtained as follows: for the optimal pressure of 1.07 Pa (see **Fig. 9**), we combine the data of **Figs. 6(b)** and **8(b)** by eliminating the power. Thus, the  $H^-$  and  $D^-$  ion densities versus the cold electron temperature are obtained as in **Fig. 14**. Then, we average the negative ion densities within 0.1 eV intervals (see grid lines in **Fig. 14**). From the resultant **Fig. 13(c)**, it is deduced that the cold electron temperature that yields negative ions lies between 0.5 and 0.9 eV in  $H_2$  and between 0.7 and 1.1 eV in  $D_2$ . According to **Figs. 13(a)** and **13(b)**, these values correspond to the cold electrons that participate to DEA with  $H_2$  and  $D_2$  molecules heated at the vibrational levels  $v \geq 7$  and  $v \geq 9$ , respectively.

However, although it is seen that the higher DEA cross sections and the span of the cold electron temperature in  $H_2$  may favor the negative ion production, this may be partially compensated for the lower cold electron density in the  $H_2$  plasma, compared to the  $D_2$  plasma, as it has been shown in section IVA). This could explain the quite close densities of  $H^-$  and  $D^-$  ions shown in **Fig. 8** as opposed to the apparent higher  $H^-$  ion density in **Fig. 11(a)** where any difference in the cold electron densities has been eliminated. Finally, this concept is in line with the lower ratio of the negative ion to cold electron density, established by **Fig. 9**. Namely, this ratio becomes higher in the  $H_2$  plasma than in the  $D_2$  plasma since the numerator is almost constant whereas the denominator lower by a factor higher than  $\sqrt{2}$  (**Fig. 12**). Based on **Fig. 9(b)**, a ratio  $\sim 0.225$  in  $H_2$  versus  $\sim 0.125$  in  $D_2$  has been mentioned in section III (at 1.07 Pa and 0.3 to 0.4 kW), i.e., 1.8 times higher in  $H_2$ . For the same conditions, **Fig. 12** gives an average cold electron density  $\sim 1.77$  times higher in the  $D_2$  plasma.

### C) (Ro)vibrational heating and higher energy part of EEDFs

The present work provides data on the EEDFs but not on the (ro)vibrational heating of the two plasmas. Hence, DEA cross sections and cold electron densities/energies alone, fail to describe the entire DEA process. Direct measurements of the vibrational distribution functions (VDFs) under similar to the present experimental conditions are in progress. Our results in the  $D_2$  plasma have already been published [50], but their correlation with the present results will be realized when the VDFs in  $H_2$  plasma will also be available from our ongoing experiments. However, **Table IV** categorizes the main reactions that lead to the  $H_2$  and  $D_2$  molecules excitation and de-excitation, and they can be correlated with the results of the present work.

Reactions **R43** and **R44** are recognized as the principal ones, and their cross sections are given in **Figs. 15(a)** and **15(b)**. A direct comparison with **Fig. 7** shows that the hot populations produced in both ECR plasmas have temperatures that lie above the threshold energy of the two reactions. It is repeated that the present measurements refer to the production region of the source, i.e., downstream of the ECR zones, which means that in the ECR zones hot electrons should obtain even higher energies and densities. Thus,  $H_2$  and  $D_2$  gases can be heated vibrationally in the ECR zones efficiently.

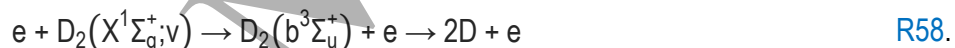
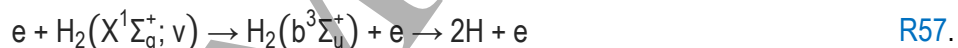
**Fig. 15(c)** compares these cross sections of the reactions **R43** and **R44** for a given electron energy close to their peak (40 eV) as a function of the final vibrational level. The values of the two cross sections are approaching each other as the vibrational level increases, i.e., at the levels where DEA becomes more efficient;  $v \geq 7$  as

discussed in section IVB) for the optimal pressure of 1.07 Pa. Thus, according to section IVB), the interplay between the lower energy part of the EEDFs and the DEA cross sections remains the main reason for the higher negative ion yield in the H<sub>2</sub> plasma than in the D<sub>2</sub> plasma at a given plasma density. In parallel, in both the plasmas, higher hot electron density may lead to higher density of each vibrational level, and thus to higher density of the negative ions. This is probably what makes the linear dependence seen in **Fig. 11(b)**. Nevertheless, the negative ion destruction processes should also be considered.

#### D) Negative ion destruction reactions

The H<sup>-</sup> and D<sup>-</sup> negative ion destruction reactions may be direct (**Table III**) or indirect in terms of molecular relaxation (**Table IV**). Among the former, associative detachment (AD: **R13, R14**) and mutual neutralization (MN: **R25–R40**) are identified as the dominant ones in the present source [53]. Regarding the molecular relaxation, it is assumed that the V–t process (R51, R52) is the principle one. In further restricting the analysis to the AD and V–t reactions, a simplistic consideration of negative ion destruction may be derived.

Thus, the rates for both reactions are sensitive to the atomic density which depends both on the gas pressure and the injected MW power, while they could be associated with the limitations in the H<sup>-</sup> and D<sup>-</sup> ion production and as well as with the optima seen in **Figs. 8-10**. In low temperature plasmas, one of the most important electronically inelastic process for the formation of neutral fragments is the excitation of the repulsive b<sup>3</sup>Σ<sub>u</sub><sup>+</sup> state (**R57** and **R58**).



Below about 12 eV, this process is the only mechanism for dissociation of H<sub>2</sub> or D<sub>2</sub> into neutral fragments [81,82] and based on the presents EEDFs (**Figs. 4** and **5**) this process should be active in our source.

In ECR sources [37,38,53] operating with hydrogen, an increase in the atomic density and a decrease in the atomic-to-molecular density for increasing pressure have been reported, whereas the latter was found to increase for increasing power [53]. At the same time, AD and MN reaction rates have been found to increase with hydrogen pressure [53,69]. These findings are consistent with **Fig. 10(a)** where the H<sup>-</sup> and D<sup>-</sup> ion production is restricted for increasing pressure. The parallel increase of the plasma density (**Fig. 2**) leads to the optima of the ratio in **Fig. 10(b)**.

Finally, regarding the isotope effect between **R57** and **R58**, the atomic-to-molecular density ratio is found to be constantly higher in the case of D<sub>2</sub> plasmas, both by means of experiments [8,28,39] and theoretical analyses [13,33]. In the light of recent calculations [81,82], the cross sections leading from the v'' = 0 vibrational level to the ground state display only a small isotope effect. Thus, the commonly observed higher atomic density in D<sub>2</sub> plasmas could be justified by the difference in the transport properties of H and D atoms [83] and points to more

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intense AD and MN losses in D<sub>2</sub> plasmas, in agreement with the lower negative ion density for a given plasma density shown in Fig. 11(a).

## Conclusions

The present report is devoted to the study of H<sub>2</sub> and D<sub>2</sub> ECR-driven plasmas oriented to negative ion sources. The main claim of the article is the investigation of the isotope effect with respect to main plasma features including the electron energy distribution functions and the negative ion densities. The following statements recap the principal similarities and differences between the H<sub>2</sub> and D<sub>2</sub> plasmas, as they have been ensued from this comparative study. Thus, two electron populations, quasi-Maxwellian, are produced, independently of the gas, the pressure, and the MW power employed. The cold electron population is constantly higher in the D<sub>2</sub> plasma, and this is attribute to the higher confinement time of positive ions in the case of deuterium. H<sup>-</sup> and D<sup>-</sup> negative ion densities are not substantially different in the two plasmas under the same operating conditions, although the H<sup>-</sup> negative ion yield is higher for a given plasma density. A strong isotope effect exists when the negative ion to electron density ratio is considered, and the latter may be up to 80% higher in the H<sub>2</sub> plasma. H<sup>-</sup> and D<sup>-</sup> negative ions are produced in the plasma volume through dissociative attachment of cold electrons onto vibrationally excited molecules. Finally, similar optimal operational windows for enhanced negative ion yield do exist in both gases, as a compromise between production and destruction processes.

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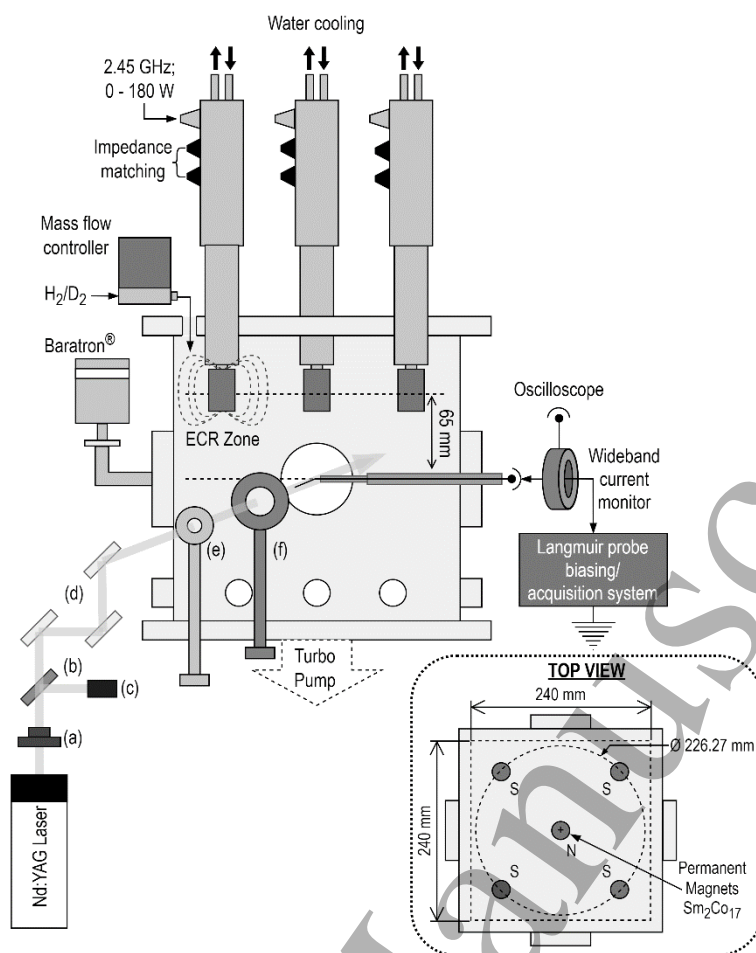
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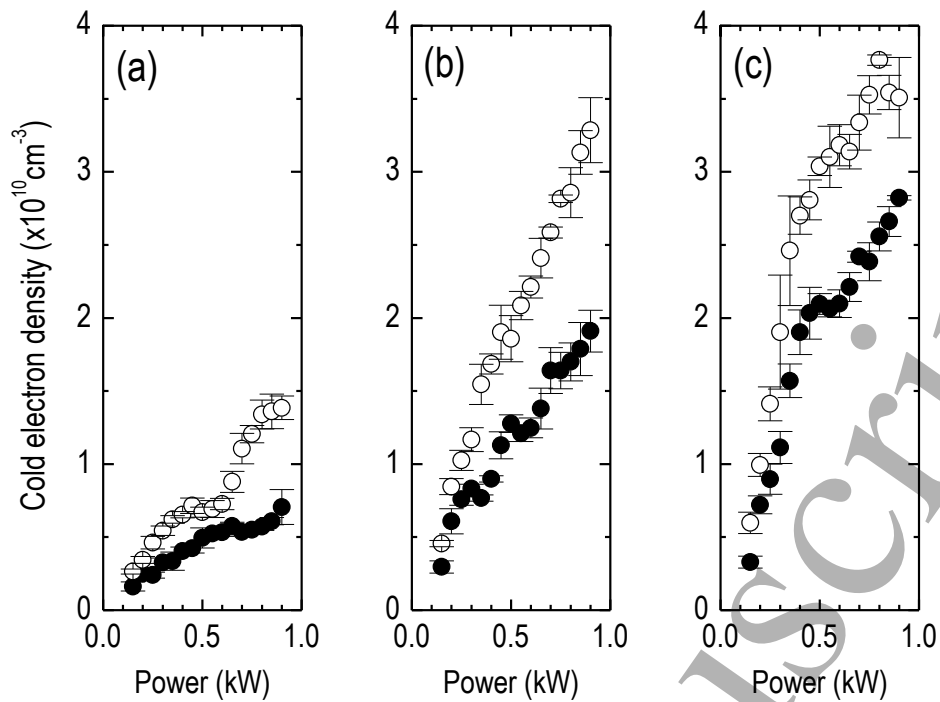
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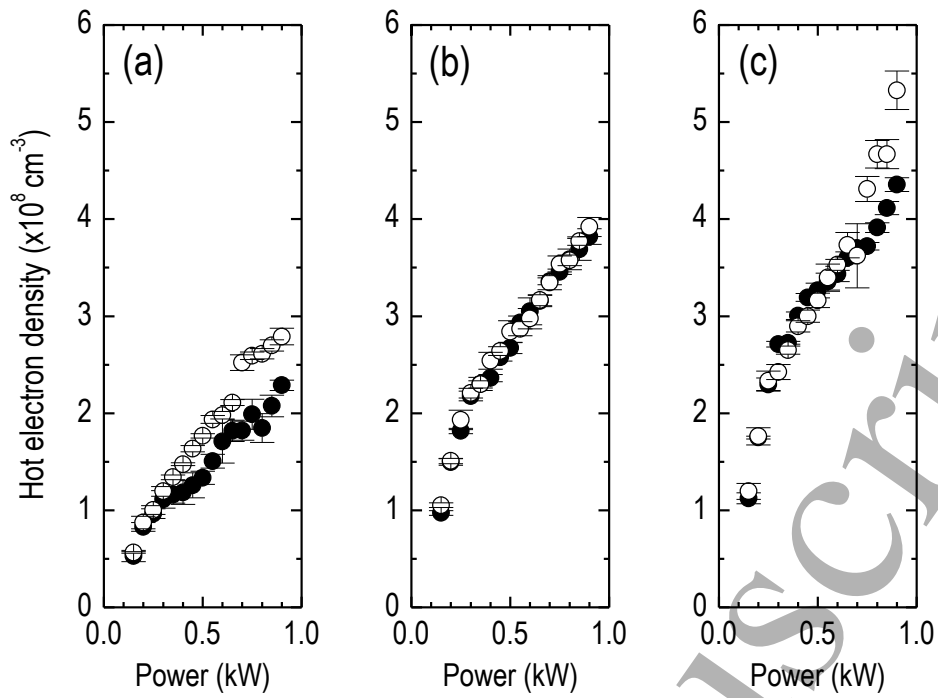
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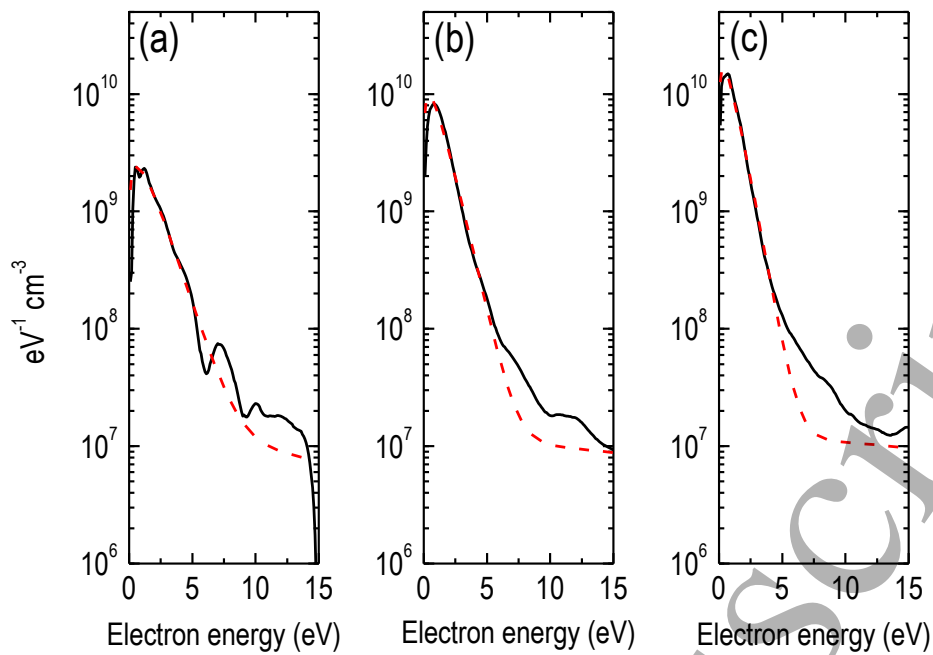
**Figure 1.** Conceptual design of the experimental setup depicting the ECR-driven source Prometheus I and the diagnostics installed for the present work (electrostatic probe and laser photo-detachment). (a) half wave plate on a precision rotation mount; (b) beam splitter; (c) laser beam dump; (d) mirrors; (e) Ø5 mm cylindrical diaphragm; (f) pyroelectric laser energy sensor (removable). The inset depicts the distribution of the ECR modules.



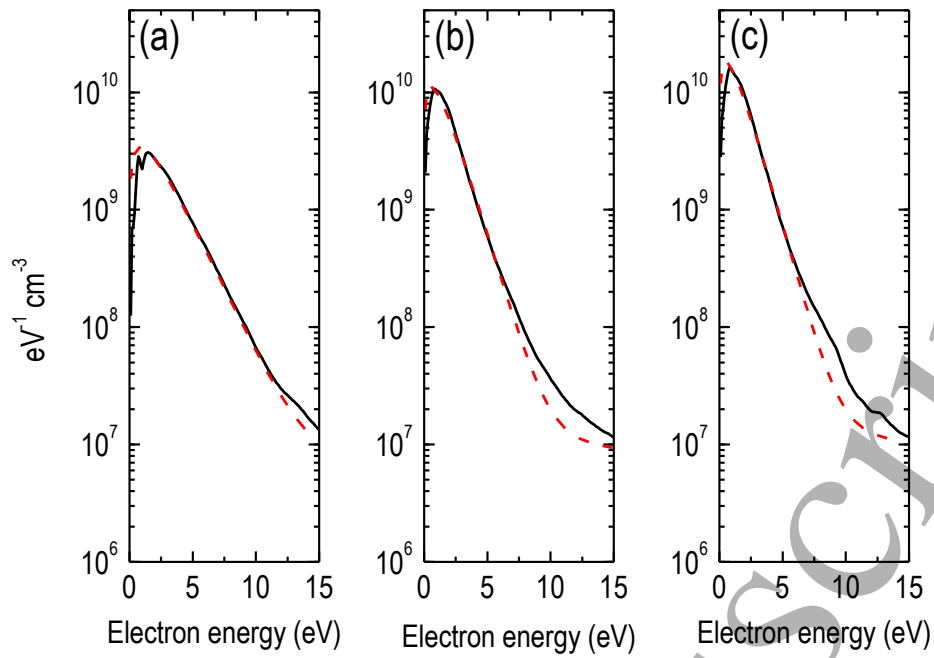
**Figure 2.** Cold electron density as a function of the MW power at (a) 0.53 Pa, (b) 1.07 Pa, and (c) 1.60 Pa. Solid circles:  $\text{H}_2$  plasma. Open circles:  $\text{D}_2$  plasma. Mean values and standard deviations are derived from four series of experiments (2 sets on 2 different dates).



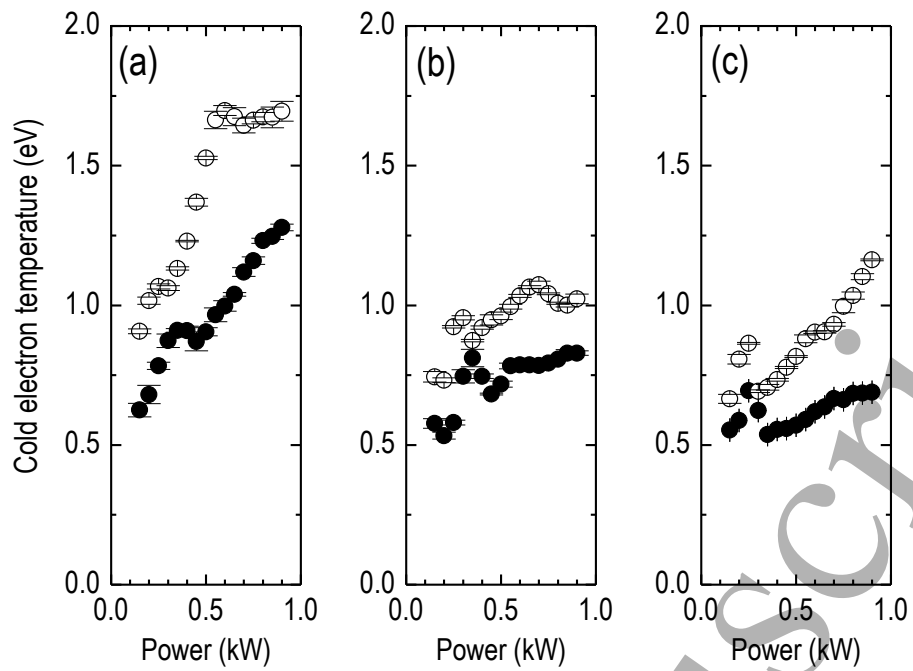
**Figure 3.** Hot electron density as a function of the MW power at (a) 0.53 Pa, (b) 1.07 Pa, and (c) 1.60 Pa. Solid circles:  $\text{H}_2$  plasma. Open circles:  $\text{D}_2$  plasma. Mean values and standard deviations are derived from four series of experiments (2 sets on 2 different dates).



**Figure 4.** Representative EEDFs from the H<sub>2</sub> ECR plasmas. **(a)** 0.53 Pa; 0.75 kW. **(b)** 1.07 Pa; 0.75 kW. **(c)** 1.60 Pa; 0.75 kW. Solid-black lines: Druyvesteyn method. Dashed-red lines: bi-Maxwellian assumption.

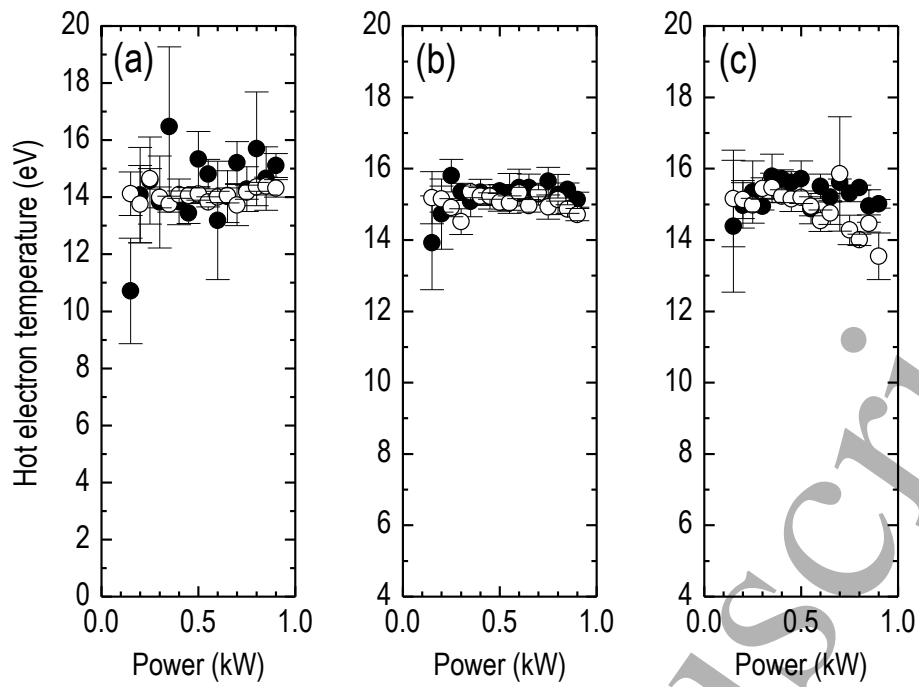


**Figure 5.** Representative EEDFs from the  $D_2$  ECR plasmas. **(a)** 0.53 Pa; 0.75 kW. **(b)** 1.07 Pa; 0.75 kW. **(c)** 1.60 Pa; 0.75 kW. Solid-black lines: Druyvesteyn method. Dashed-red lines: bi-Maxwellian assumption.

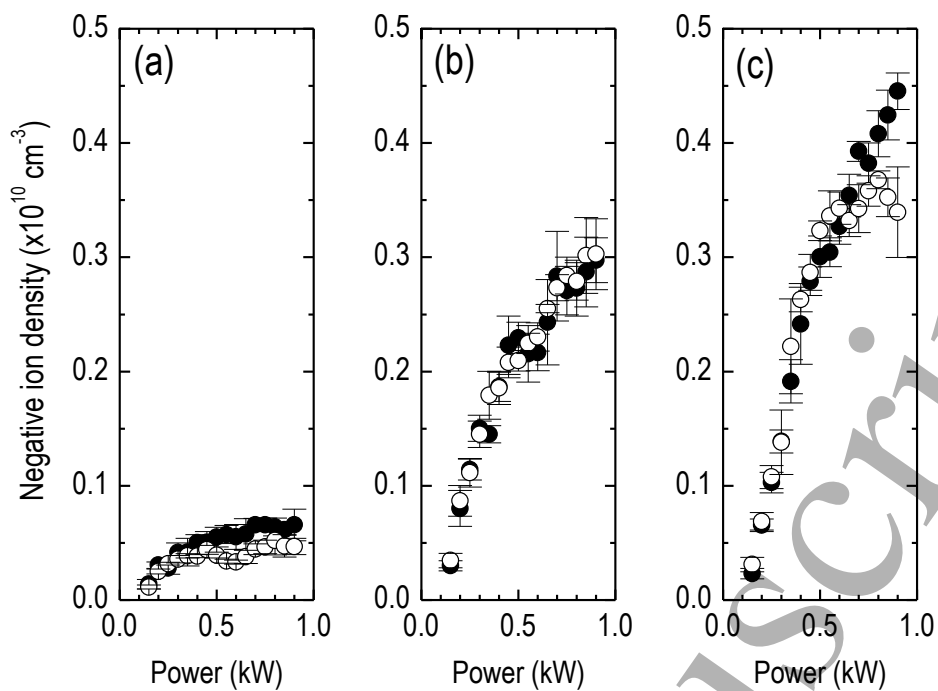


**Figure 6.** Cold electron temperature as a function of the MW power at (a) 0.53 Pa, (b) 1.07 Pa, and (c) 1.60 Pa.

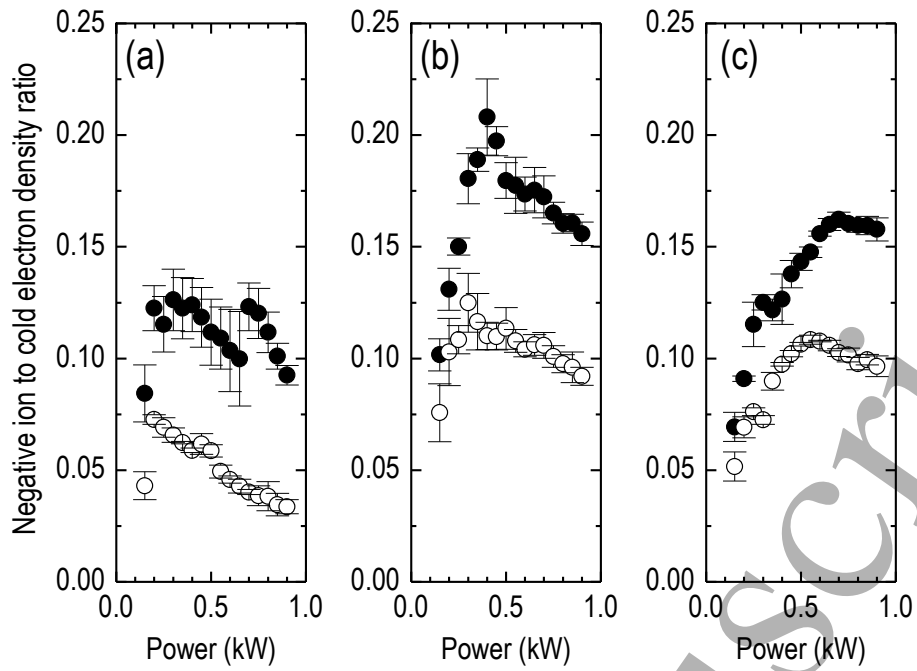
Solid circles: H<sub>2</sub> plasma. Open circles: D<sub>2</sub> plasma. Mean values and standard deviations are derived from four series of experiments (2 sets on 2 different dates).



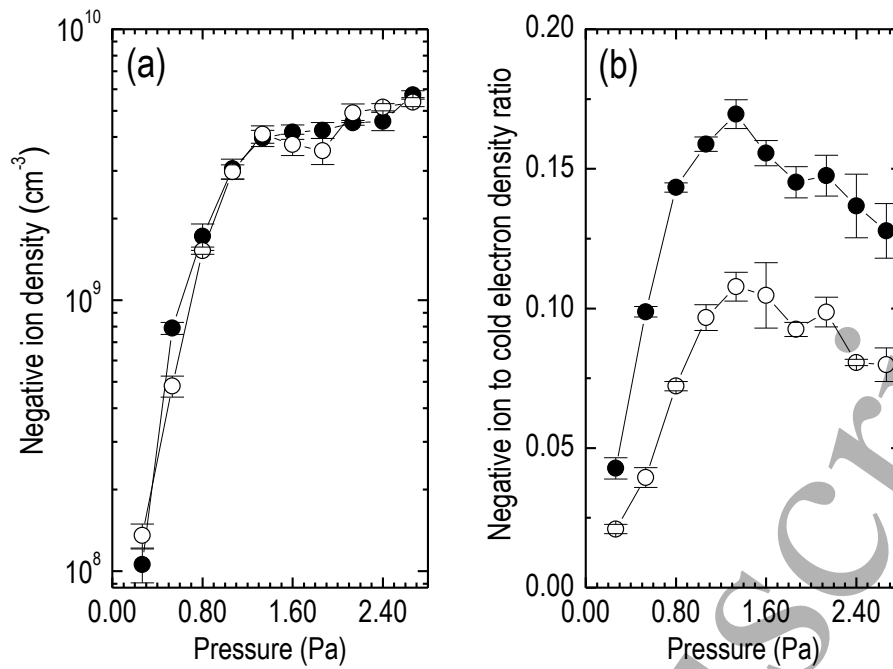
**Figure 7.** Hot electron temperature as a function of the MW power at (a) 0.53 Pa, (b) 1.07 Pa, and (c) 1.60 Pa. Solid circles: H<sub>2</sub> plasma. Open circles: D<sub>2</sub> plasma. Mean values and standard deviations are derived from four series of experiments (2 sets at 2 different dates).



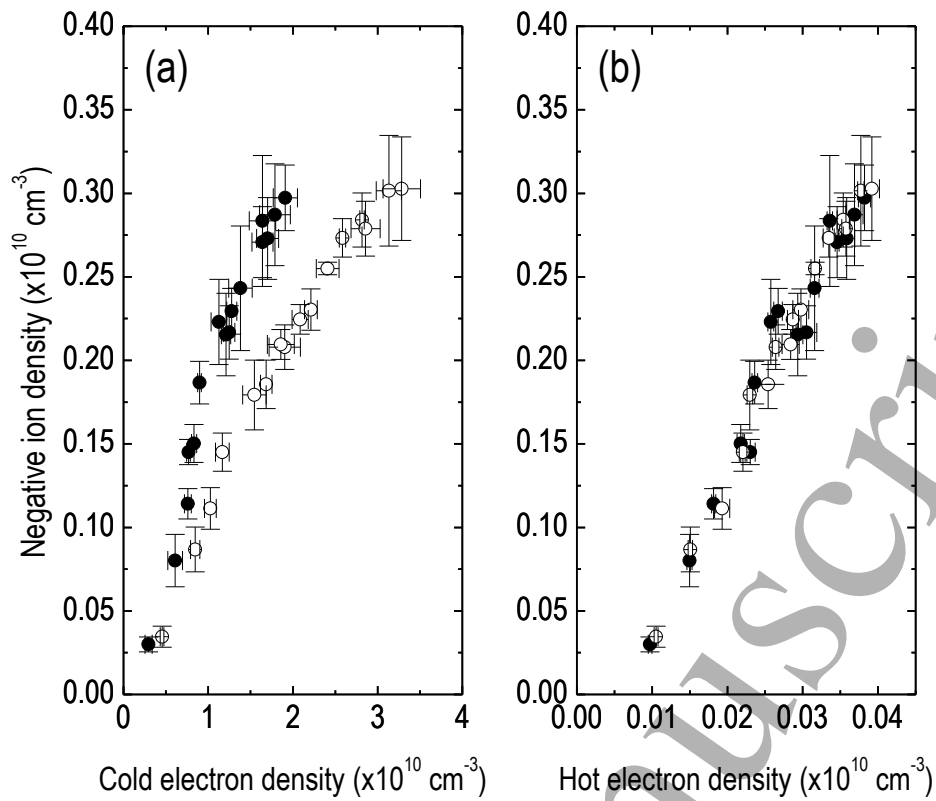
**Figure 8.** Negative ion density as a function of the MW power at (a) 0.53 Pa, (b) 1.07 Pa, and (c) 1.60 Pa. Solid circles:  $\text{H}_2$  plasma. Open circles:  $\text{D}_2$  plasma. Mean values and standard deviations are derived from four series of experiments (2 sets on 2 different dates).



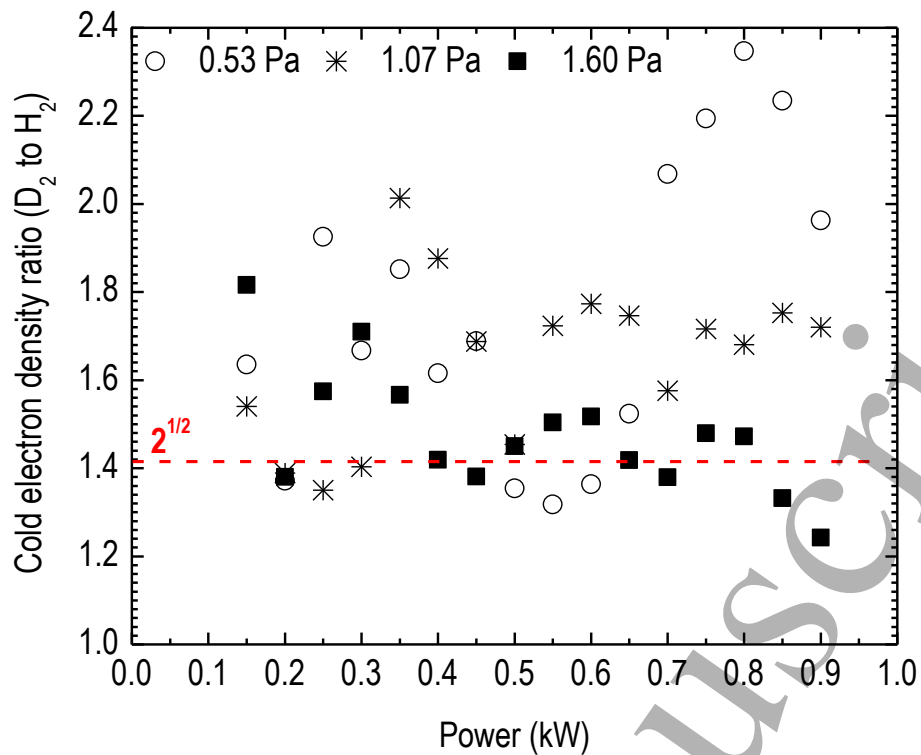
**Figure 9.** Negative ion to cold electron density as a function of the MW power at (a) 0.53 Pa, (b) 1.07 Pa, and (c) 1.60 Pa. Solid circles: H<sub>2</sub> plasma. Open circles: D<sub>2</sub> plasma. Mean values and standard deviations are derived from four series of experiments (2 sets on 2 different dates).



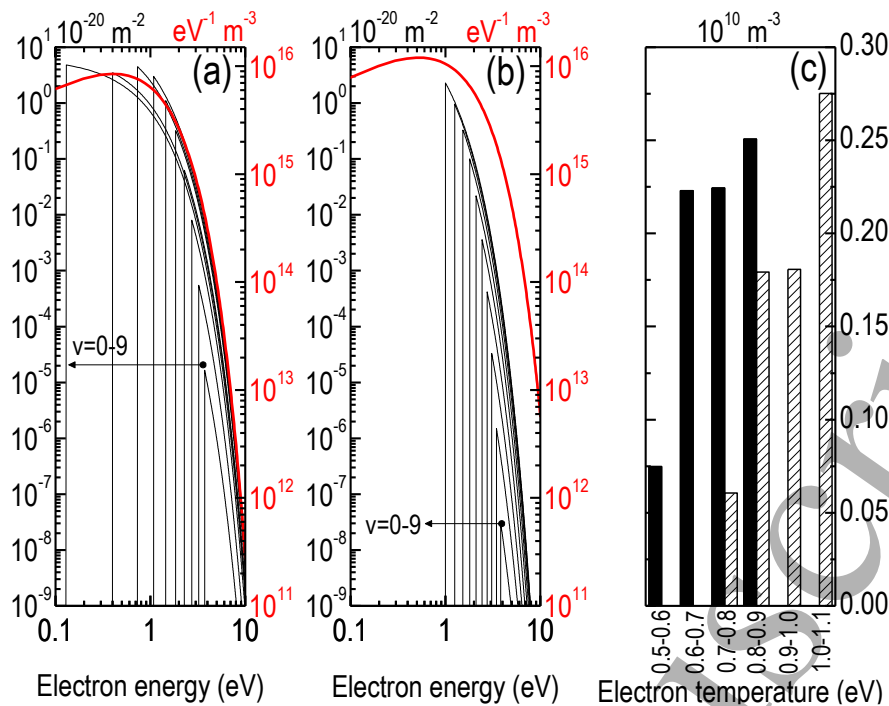
**Figure 10.** (a) Negative ion density and (b) Negative ion to cold electron density, as a function of the working pressure (0.9 kW). Solid circles:  $\text{H}_2$  plasma. Open circles:  $\text{D}_2$  plasma. Mean values and standard deviations are derived from four series of experiments (2 sets on 2 different dates).



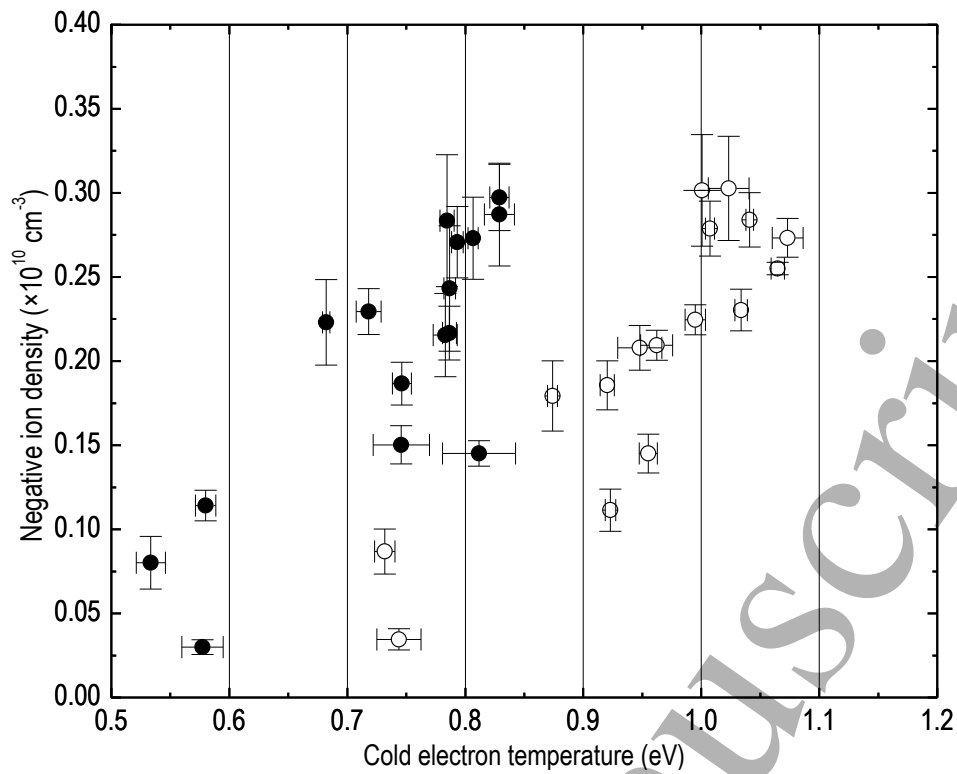
**Figure 11.** Negative ion density as a function of the density of the: **(a)** cold electron population, **(b)** hot electron population. Solid circles:  $\text{H}_2$  plasma. Open circles:  $\text{D}_2$  plasma. Mean values and standard deviations are derived from four series of experiments (2 sets at 2 different dates), 1.07 Pa.



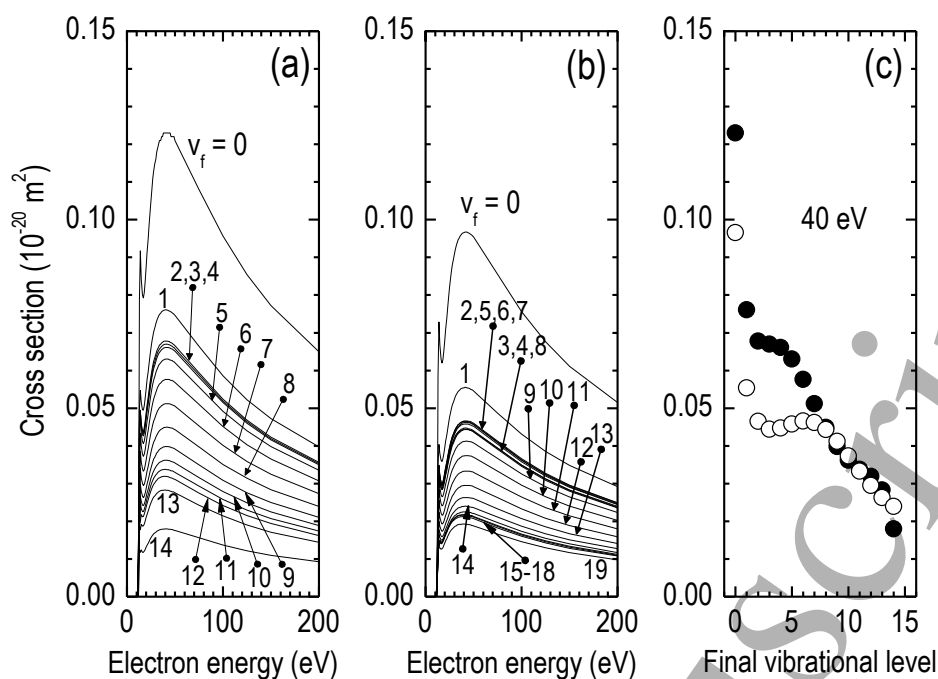
**Figure 12.** Ratio of the cold electron densities measured in the D<sub>2</sub> plasma to the cold electron densities measured in the H<sub>2</sub> plasma, from Fig. 2, as a function of the MW power at three different pressures. The level of  $\sqrt{2}$  is given for comparison reasons; see text.



**Figure 13.** Cross sections of the reactions **(a)** R1/Table III (H<sub>2</sub> case) and **(b)** R2/Table III (D<sub>2</sub> case). These curves are plotted according to the equation given in Ref. [62] and the available data in Table I of Ref. [61], following the APS permission under the license number RNP/23/MAR/064140. The red curves correspond to indicative EEDFs of the cold electron population (Figs. A1 and A2; Appendix). **(c)** Histograms of the average values of the negative ion densities over 0.1 eV temperature intervals of the cold electron population; H<sub>2</sub> (solid bars) and D<sub>2</sub> (patterned bars); 1.07 Pa.



**Figure 14.** Negative ion density as a function of the cold electron temperature; the data of Figs. 6(b) and 8(b) are combined, by eliminating the power. The grid lines define the temperature intervals where the negative ion density is averaged for getting the histograms of Fig. 13(c). Solid circles: H<sub>2</sub> plasma. Open circles: D<sub>2</sub> plasma.



**Figure 15.** Cross sections of the reaction numbered as (a) R41. ( $\text{H}_2$ ) and (b) R42. ( $\text{D}_2$ ), in Table IV. The initial vibrational level is  $v_i = 0$ . These curves are plotted according to the available data in the online Tables XIX(a1) and XIX(b1) of Ref. [62], following the permission of Prof. Dr. R. Celiberto et al. (c) Comparison of the cross-section values of  $\text{H}_2$  (solid circles) and  $\text{D}_2$  (open circles) for increasing vibrational level, at an electron energy around 40 eV where the curves peak. Data are collected from Ref. [62].

**Table I.** Tabulated characteristics of the ECR sources quoted in the text. (Ext.: Extraction aperture; NI: No Information; NA: Not Applicable).

ECR Source	Dimensions	ECR Coupling	Power (kW)	Pressure (Pa)	Gas	Ext.	Te (eV)	$n_{e(cold)}$ ( $m^{-3}$ )	$n_{H^-}$ ( $m^{-3}$ )	Extr. Current (mA)
ECR source with driven plasma rings	Aluminum; $\varnothing 130$ mm $\times$ 80 mm	External magnetic discs; 2.45 GHz	max. 0.25 (experiments throughout the range)	0.02 – 0.07	H <sub>2</sub> / D <sub>2</sub>	✓	50 – 60	$5 \times 10^{16}$ (0.026 Pa; H <sub>2</sub> [36]).	NI	$\leq 4.7$ (H <sub>2</sub> ) $\leq 3.1$ (D <sub>2</sub> ) (0.2 kW)
HOMER	Stainless steel; $\varnothing 150$ mm $\times$ 310 mm (prolonged to 410 mm in [38])	Helmholtz coils; 2.45 GHz	max. 1 (For experiments: 0.2–0.5 [37])	0.3 – 3	H <sub>2</sub> / D <sub>2</sub>	✗	0.6 – 1; NI	$10^{16} - 10^{17}$	$\leq 3.9 \times 10^{15}$ (H <sub>2</sub> ) [37] Above MoLa (0.3 kW, 0.3 Pa) [39]: $\leq 1.4 \times 10^{15}$ (H <sub>2</sub> ), $\leq 1.45 \times 10^{15}$ (D <sub>2</sub> )	NA
Camembert III	Stainless steel; $\varnothing 440$ mm $\times$ 450 mm	7 ECR modules & multicusp field configuration; 2.45 GHz	max. 1.2 (for experiments: 0.5 & 1 [42], 0.9 [44], 1.05 [43])	0.13 – 1.07 [42–44]	H <sub>2</sub>	✓	Within 0.2 – 1.3	In the range of $10^{14} - 10^{16}$	$\leq 2.6 \times 10^{15}$	$\leq 0.25$ (0.9 kW [44] and 1 kW [42], 0.27 Pa)
ROSAE III	Pyrex cylinder of $\varnothing 152$ mm $\times$ 214 mm housed in a stainless steel cylinder	4 ECR modules; 2.45 GHz	max. 1.2 (For experiments: 0.76 or 0.2 [46] & 1 [47])	0.33 or 1.3 [46]	H <sub>2</sub>	✗	0.9; 11 or 2; 6	0.13 $\times 10^{16}$ or $1.4 \times 10^{16}$	0.06 $\times 10^{15}$ or $1.7 \times 10^{15}$	NA
	Quartz cylinder $\varnothing 152$ mm housed in a stainless steel cylinder [48]	Modified: 1 ECR module; 2.45 GHz	max. 0.2 (for experiments: 0.075 – 0.175)	0.67 [47]			1.81; 9.45	$\sim 6.5 \times 10^{15}$ (Pyrex)	$\sim 1.5 \times 10^{14}$ (Pyrex)	
SCHEME	Stainless steel; outer dim.: $\varnothing 160$ mm; inner dim. $\varnothing 124$ mm $\times$ 220 mm (quartz tube) [50]	1 ECR module; 2.45 GHz	max. 0.45 (for experiments: 0.15) [50]	0.8 [50]	H <sub>2</sub> / D <sub>2</sub>	✗	$\sim 1.5$ ; $\sim 15$	$\sim 10^{15}$	$\sim 10^{13}$ (quartz coverage – D <sub>2</sub> )	NA
PROMETHEUS I	Stainless steel; $240 \times 240 \times 240$ mm <sup>3</sup>	5 ECR modules; 2.45 GHz	max. 0.9 (experiments throughout the range)	0.13 – 2.67	H <sub>2</sub> / D <sub>2</sub>	✗	0.5 – 2; 12.5 – 17	$\leq 4.5 \times 10^{16}$ (H <sub>2</sub> ); $\leq 7 \times 10^{16}$ (D <sub>2</sub> ).	$\leq 6 \times 10^{15}$	NA

**Table II.** Tabulated information of representative experimental conditions ( $H_2 / D_2$ ).

Pressure (Pa / mTorr)	0.15 kW		0.9 kW	
	Flow rate (sccm)	Wall Temp. ( $^{\circ}C$ )	Flow rate (sccm)	Wall Temp. ( $^{\circ}C$ )
	( $H_2 / D_2$ )	( $H_2 / D_2$ )	( $H_2 / D_2$ )	( $H_2 / D_2$ )
<b>0.53 / 4</b>	6.9 / 8.6	42 / 44	7.4 / 9.2	116.5 / 128.2
<b>1.07 / 8</b>	11.8 / 15.0	41.7 / 43	12.5 / 15.3	119.3 / 120.6
<b>1.60 / 12</b>	16 / 20.1	40.8 / 41.7	16.8 / 20.7	117.4 / 122.2

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**Table III.** Reaction set for the production and destruction of negative ions (\* RX denotes: by analogy with the X reaction).

PRODUCTION			
R1.	$e + H_2(X^1\Sigma_g^+;v) \rightarrow H_2^- \rightarrow H + H^-$	Dissociative Electron Attachment: DEA	[61, 62]
R2.	$e + D_2(X^1\Sigma_g^+;v) \rightarrow D_2^- \rightarrow D + D^-$		
R3.	$e + H_2^+ \rightarrow H^+ + H^-$	Dissociative Recombination: DR	[63, 64]
R4.	$e + D_2^+ \rightarrow D^+ + D^-$		
R5.	$e + H_3^+ \rightarrow H_2^+ + H^-$	Dissociative Recombination: DR	[63]
R6.	$e + D_3^+ \rightarrow D_2^+ + D^-$		
R7.	$e + H_2(v,J) \rightarrow H^- + H^+ + e$	Polar Dissociation	[63]
R8.	$e + D_2(v,J) \rightarrow D^- + D^+ + e$		
R9.	$H_2 + H_2^+ \rightarrow H^- + H + 2H^+$	Ion-Molecule Collisions	[*R11]
R10.	$H_2 + H_2^+ \rightarrow H^- + H^+ + H_2^+$		[*R12]
R11.	$D_2 + D_2^+ \rightarrow D^- + D + 2D^+$		[63]
R12.	$D_2 + D_2^+ \rightarrow D^- + D^+ + D_2^+$		[63]
DESTRUCTION			
R13.	$H^- + H \rightarrow H_2 + e$	Associative Detachment: AD	[66]
R14.	$D^- + D \rightarrow D_2 + e$		
R15.	$H^- + H \rightarrow H_2(v) + e$	Associative Detachment (AD) with creation of vibrationally excited molecules	[67]
R16.	$D^- + D \rightarrow D_2(v) + e$		[*R15]
R17.	$H^- + H \rightarrow 2H + e$	non-Associative Detachment: non-AD	[68]
R18.	$D^- + D \rightarrow 2D + e$		[63]
R19.	$H^- + e \rightarrow H + 2e$	Electron Detachment: ED	[68]
R20.	$D^- + e \rightarrow D + 2e$		[63]
R21.	$H^- + H_2(v) \rightarrow H_2(v-2) + H + e, 2 \leq v \leq 6$	Electron Detachment in collisions with vibrationally excited molecules: EDV	[69, 70]
R22.	$D^- + D_2(v) \rightarrow D_2(v-2) + D + e, 2 \leq v \leq 6$		[*R21]
R23.	$H^- + H_2 \rightarrow H_2 + H + e$	Collisional Detachment: CD	[71]
R24.	$D^- + D_2 \rightarrow D_2 + D + e$		
R25.	$H^- + H^+ \rightarrow 2H$	[69, 72]	
R26.	$H^- + H^+ \rightarrow H + H(n=2, 3)$	[69, 73]	
R27.	$H^- + H_2^+ \rightarrow H_2 + H$	[69, 73]	
R28.	$H^- + H_2^+ \rightarrow 3H$	[69, 72]	
R29.	$H^- + H_2^+ \rightarrow H + H_2(v)$	[67]	
R30.	$H^- + H_3^+ \rightarrow 2H_2$	Mutual Neutralization: MN	[69, 73]
R31.	$H^- + H_3^+ \rightarrow 4H$		[69, 72]
R32.	$H^- + H_3^+ \rightarrow 2H + H_2(v)$	[67]	
R33.	$D^- + D^+ \rightarrow 2D$	[*R25]	
R34.	$D^- + D^+ \rightarrow D + D(n=2, 3)$	[*R26]	
R35.	$D^- + D_2^+ \rightarrow D_2 + D$	[*R27]	
			[*R28]



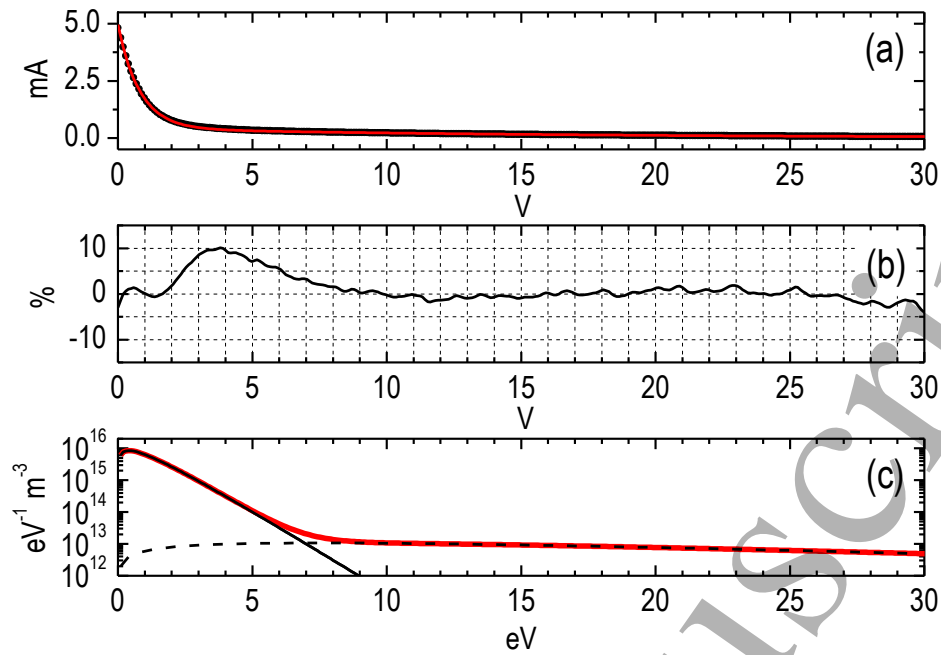
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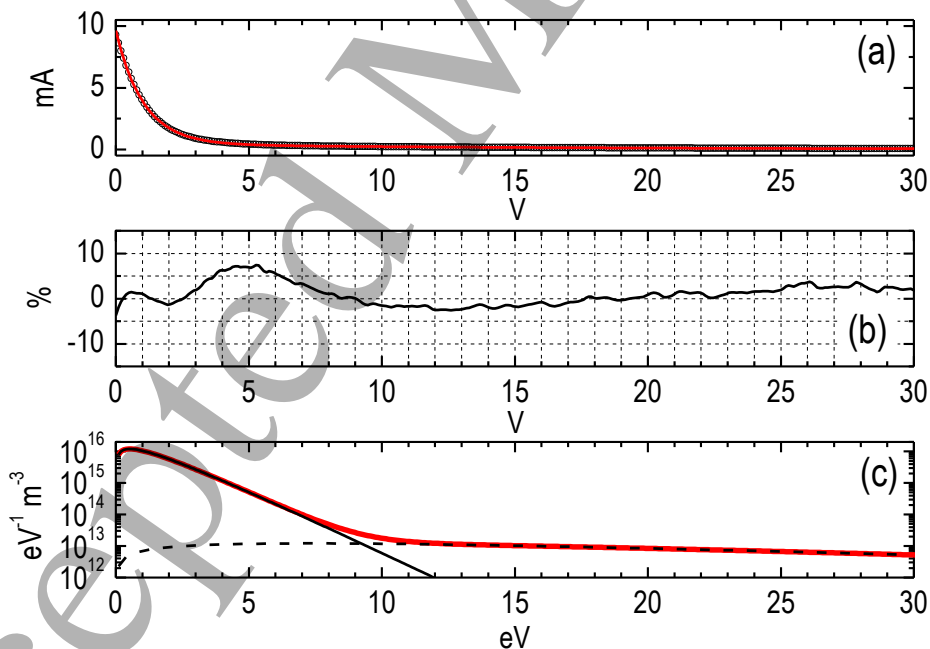
**Table IV.** Representative reactions for the population and de-excitation of vibrational states (\* RX denotes: by analogy with the X reaction).

EXCITATION		
R41.	$H_2(X^1\Sigma_g^+; v_i) + e \rightarrow H_2(X^1\Sigma_g^+; v_f) + e, v_f > v_i$	Resonant electron-vibration excitation: eV [74]
R42.	$D_2(X^1\Sigma_g^+; v_i) + e \rightarrow D_2(X^1\Sigma_g^+; v_f) + e, v_f > v_i$	
R43.	$H_2(X^1\Sigma_g^+; v_i) + e \rightarrow H_2(B^1\Sigma_u^+, C^1\Pi_u) + e \rightarrow H_2(X^1\Sigma_g^+; v_f) + e + hv, v_f > v_i$	Radiative decay and excitation: EV [62]
R44.	$D_2(X^1\Sigma_g^+; v_i) + e \rightarrow D_2(B^1\Sigma_u^+, C^1\Pi_u) + e \rightarrow D_2(X^1\Sigma_g^+; v_f) + e + hv, v_f > v_i$	
Recombinative Desorption:		
R45.	$H(\text{wall}) + H(\text{wall}) \rightarrow H_2(v)$	Langmuir–Hinshelwood [75]
R46.	$D(\text{wall}) + D(\text{wall}) \rightarrow D_2(v)$	
R47.	$H(\text{gas}) + H(\text{wall}) \rightarrow H_2(v)$	Eley–Rideal [76]
R48.	$D(\text{gas}) + D(\text{wall}) \rightarrow D_2(v)$	
R49.	$H(\text{wall}^*) + H(\text{wall}) \rightarrow H_2(v)$	'Hot-atom' (Harris–Kasemo) [77]
R50.	$D(\text{wall}^*) + D(\text{wall}) \rightarrow D_2(v)$	
Where, $H/D(\text{wall}^*)$ , refers to a "weakly bound" atom on the surface		
DE-EXCITATION		
R51.	$H_2(v_i) + H \rightarrow H_2(v_f) + H, v_f < v_i$	Vibrational-translational relaxation in collisions with atoms: V-t [69, 78]
R52.	$D_2(v_i) + D \rightarrow D_2(v_f) + D, v_f < v_i$	
R53.	$H_2(v_i) + H_2(v_j) \rightarrow H_2(v_i) + H_2(v_j-1)$	Vibrational-translational relaxation in collisions with molecules: V-T [73]
R54.	$D_2(v_i) + D_2(v_j) \rightarrow D_2(v_i) + D_2(v_j-1)$	
R55.	$H_2(v_i) + \text{wall} \rightarrow H_2(v_f), v_f < v_i$	Wall relaxation: WD [69, 79]
R56.	$D_2(v_i) + \text{wall} \rightarrow D_2(v_f), v_f < v_i$	

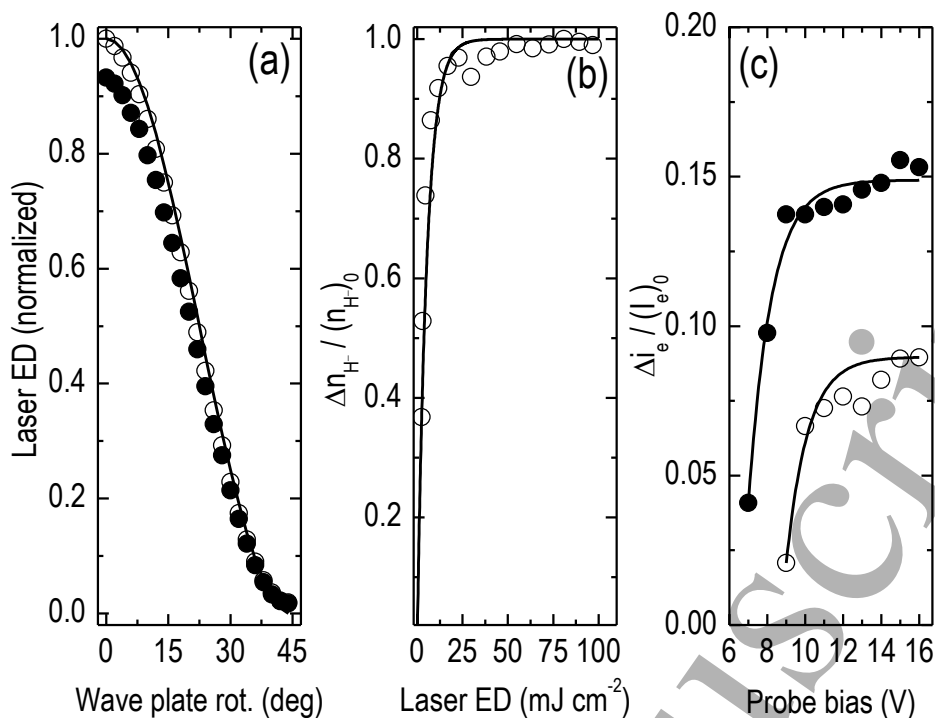
## Appendix



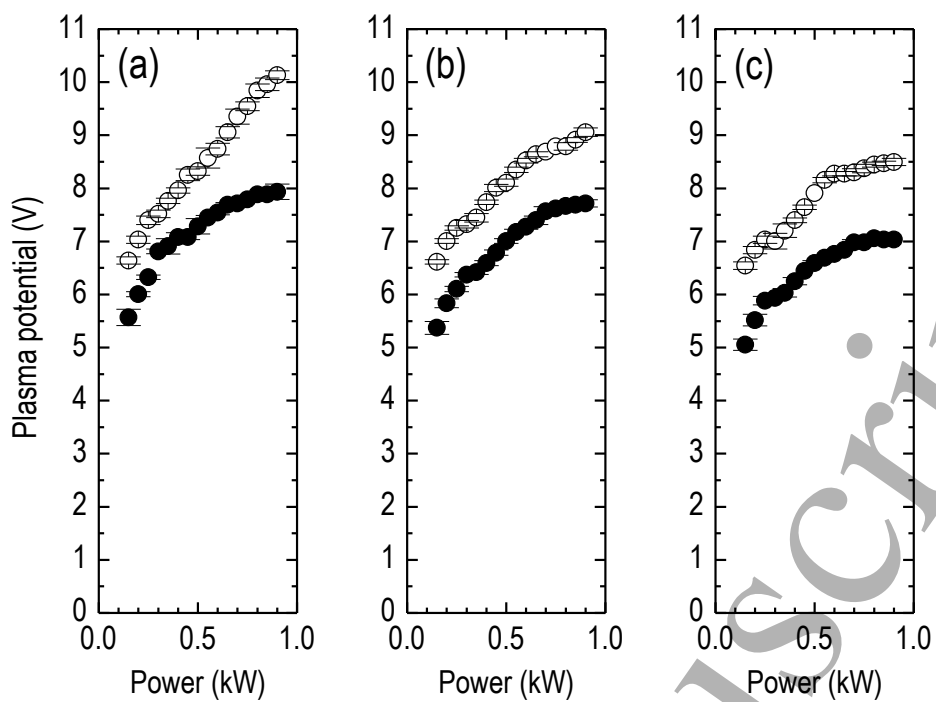
**Figure A1.** Representative example from the  $\text{H}_2$  plasma (1.07 Pa, 0.75 kW). **(a)** Bi-Maxwellian fitting (red line) to the experimentally determined electron current (black solid circles), versus the absolute value of the difference between the probe bias and the plasma potential. **(b)** Percentage of the residuals of the fitting process. **(c)** EEDF (red line) based on the bi-Maxwellian assumption; cold population part (black solid line; 0.81 eV); hot population part (black dashed line; 15.32 eV).



**Figure A2.** Representative example from the  $\text{D}_2$  plasma (1.07 Pa, 0.75 kW). **(a)** Bi-Maxwellian fitting (red line) to the experimentally determined electron current (black open circles), versus the absolute value of the difference between the probe bias and the plasma potential. **(b)** Percentage of the residuals of the fitting process. **(c)** EEDF (red line) based on the bi-Maxwellian assumption; cold population part (black solid line; 1.04 eV); hot population part (black dashed line; 14.65 eV).



**Figure A3.** (a) Normalized attenuation curves of the laser beam energy density (ED). Line: Malus' law; Open circles: measurements in front of a viewport; Solid circles: measurements behind a single glass viewport. (b) Ratio of the photo-destroyed negative ion density  $\Delta n_{H^-}$  to the saturation density  $(n_{H^-})_0$ , as a function of the laser beam ED. Line: theory [56]; Open circles: experiments at 2.0 Pa of  $\text{H}_2$  and 0.9 kW. (c) Ratio of the photodetachment signal peak (due to the instantaneously photodetached electrons) ( $\Delta i_e$ ) to the steady state electron current  $(I_e)_0$ , as a function of the probe bias voltage. Open circles: 1.60 Pa of  $\text{D}_2$  and 0.9 kW; Solid circles: 1.60 Pa of  $\text{H}_2$  and 0.9 kW. Lines: exponential fitting.



**Figure A4.** Plasma potential as a function of the MW power at (a) 0.53 Pa, (b) 1.07 Pa, and (c) 1.60 Pa. Solid circles: H<sub>2</sub> plasma. Open circles: D<sub>2</sub> plasma. Mean values and standard deviations are derived from four series of experiments (2 sets at 2 different dates).