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Detection of water molecules in inert gas based plasma by the ratios of atomic spectral lines

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Abstract

A new approach is considered to detect the water leaks in inert plasma-forming gas present in the reactor chamber. It is made up of the intensity ratio of D_α and H_α spectral lines in combination with O, Ar and Xe lines intensity. The concentrations of H_2O, O, H and D particles have been measured with high sensitivity. At the D_2 admixture pressure $p_{D_2} = 0.025$ mbar, we used the acquisition time of 10 s to measure the rate of water molecules injected from the outside, $\Gamma^0 = 1.4 \cdot 10^{-9}$ mbar $\cdot$ m$^3 \cdot$ s^{-1}, and the incoming water molecules to plasma, $\Gamma = 5 \cdot 10^{-11}$ mbar $\cdot$ m$^3 \cdot$ s^{-1}. The scaling proves that at small D_2 admixtures (10^{-4} mbar), the leaks with the rates $\Gamma^0 \approx 6 \cdot 10^{-12}$ mbar $\cdot$ m$^3 \cdot$ s^{-1} and $\Gamma \approx 2 \cdot 10^{-13}$ mbar $\cdot$ m$^3 \cdot$ s^{-1} can be detected and measured. The difference between Γ^0 and Γ values is due to the high degree of H_2O dissociation, which can be up to 97–98%.

Keywords: optical actinometry, low-temperature plasmas, plasma chemistry

(Some figures may appear in colour only in the online journal)

1. Introduction

Studies and engineering of thermonuclear reactors needs to control for the possible presence of water and water fragments in plasma as a result of particle penetration through the defects of water cooled chamber walls. The scale and complication of experimental reactors grow in parallel with the reliability requirements. Alternatively, diagnostic tools need to be technically simple in order to be matched with the reactor, where we have limited access to plasma media. This is why the noninvasive distant spectral analysis of plasma spontaneous emissions appears to be an attractive method. In last decade, several versions of emission spectroscopy techniques concerned with this problem were elaborated. A brief review of these approaches is presented in [1–6]. The best sensitivity of the leak monitoring at the level of 10^{-7} Pa $\cdot$ m$^3 \cdot$ s^{-1} (10^{-7} Pa $\cdot$ m$^3 \cdot$ s$^{-1} = 10^{-9}$ mbar $\cdot$ m$^3 \cdot$ s$^{-1} = 10^{-6}$ mbar $\cdot$ l $\cdot$ s^{-1} $= 10^{-7}$ W or ~10^{13} molecules s^{-1}) was demonstrated by means of a combination of the probe and absolute optical measurements or by optical actinometry techniques, whereby the sensitivity specified by project ITER [7], which is presently under construction, was attained. The actinometry seems to be more simple and convenient because no absolute glow intensity and probe measurements are required in this case. It was recently extended for concurrent absolute density measurements of H_2O, OH, O, and H particles [8, 9].

In the present work, we provide a new technique for water and water fragments monitoring with a purpose of applying this to thermonuclear reactors. This technique uses unstable particles as intermediate actinometers. Specifically, in these machines, the D_2 and D molecules can exist as active or residual particles. The influence of H_2 and H_2O admixtures on D_α and H_α spectral line intensities was recently observed by Kurnaev and co-workers [10] in experiments with electron beam sustained plasma. We discuss the possibility to use this effect for particle density quantitative monitoring.

2. Experimental setup

The experimental scheme (figure 1) is basically the same as described in [2, 8]. The stainless chamber, *1* of 22 l in volume,

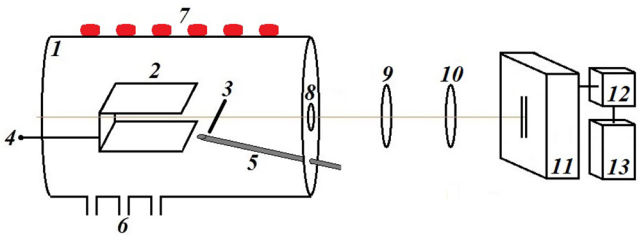

Figure 1. Experimental setup of the discharge device. For legend, see the text.

houses the discharge with tungsten hollow cathode *2* in the form of a cavity ($z \times y \times x = 100 \times 50 \times 10\,\mathrm{mm}^3$) with an open end face of $100 \times 10\,\mathrm{mm}^2$ in sizes. The tungsten sides of the cathode are externally covered with ceramic plates. Anode *3* is a tungsten wire 1.5 mm in diameter taut parallel to the z-axis of the cathode at a distance of 15 mm from its edge. Such discharge geometries were used for modeling the area of ITER wall blanket elements joint. In this study, the discharge current is 280 mA (*4*—HV supply).

Water vapor is fed into the discharge device at position *5* at a distance of a few centimeters from the anode. The preliminary prepared buffer helium gas containing admixtures of actinometers (He:Xe:Ar = 99:1:1) is fed into the vacuum chamber from container via leak (*6*—represents evacuation and filling ports). In the present work, the pressure $p_{(\mathrm{He+Ar+Xe})} = 0.6\,\mathrm{mbar}$. Deuterium and water molecules can also be fed separately from their containers through fine leaks in *6*. The filling pressure of inert gas mixture and the partial pressure of molecular additives have been controlled individually. The residual pressure of the evacuated chamber is $6 \cdot 10^{-5}$ mbar. The chamber walls can be heated up to 300 C to remove adsorbed water molecules (*7*—heater).

The plasma emission was analyzed by a monochromator *11* (Model MDR-204) with a diffraction grating of 1500 lines mm^{-1} (relative aperture 1:6, reverse linear dispersion 1.57 nm mm^{-1}). The light detector (phototube *12*) signal was processed online numerically. *8*— represents a flange with quartz window, *9* and *10*—show a system of lenses and *13*—is the recording and processing electronics.

3. Measurement method

The most prominent fragments of the discharge emission spectra in the range 300–900 nm are related to the bands of He, Ar, Xe, O, H, D atoms and hydroxyl OH. The actinometry technique [11] was used to measure the particle concentrations. The concentrations N_X of the particles X being measured are related to the known concentration N_A of the actinometer particles A added. The particles X and A make up an actinometric pair. The relationship between their concentrations is established by comparing the glow intensities I of the particles:

$$I_{X,A} = C_{X,A} h\nu_{X,A} A_{X,A} k_{X,A} N_{X,A} (Q_{X,A} + (\tau_{X,A})^{-1})^{-1}. \quad (1)$$

Here, $k_{X,A}$ are the rates of excitation of the upper transition levels from the ground states per particle by electrons, $Q_{X,A} = \Sigma q_{X,A} N_i$ are the frequencies of the upper level decays as a result of collisions with the particles N_i with the rate constants $q_{X,A} = \langle \nu_{X,A} \sigma_{X,A} q \rangle$, $A_{X,A}$ are the Einstein coefficients of the transitions, $C_{X,A}$ are coefficients defined by the optical scheme, and $\tau_{X,A}$ are the radiation lifetimes of the emitting states.

Table 1. The actinometric pairs.

Actinometric pair	States	E_t, eV	λ, nm
$X_1 = H_2O$, $A_1 = Xe$	X_1^*—not observed, the 'hot' bands of OH are used [1]	9.0	312.5
	$A_1^* = Xe(^2P^0_{3/2})6p$	9.8	823.16
$X_2 = O$, $A_2 = Xe$	$X_2^* = O(3p^5P)$	10.7	777.19
	$X_2^{**} = O(3p^3P)$	10.9	844.64
	$A_2^* = Xe(^2P^0_{3/2})6p$	9.8	823.16
$X_3 = H$, $A_3 = Ar$	$X_3^* = H(^2S_{1/2})3s$	12.1	656.27
	$A_3^* = Ar(2P^0_{3/2})4p$	13.3	751.46
$X_4 = D$, $A_4 = Ar$	$X_4^* = D(^2S_{1/2})3s$	12.1	656.09
	$A_4^* = Ar(2P^0_{3/2})4p$	13.3	751.46

In this study, we determine the concentrations of O, H, D and H_2O which will be used to implement the technique based on the ratio of D_α to H_α spectral line intensities. Following the results of [8], the chosen actinometric pairs for the measurements of O, H, and H_2O are presented in table 1. Atoms D are added as a counterpart with Ar in an actinometeric pair. Also shown are the upper excited X^*, A^* states, threshold energies E_t for their excitation, and the wavelengths for optical transitions used. For O atom measurements, two upper states X^* and X^{**} were used.

The solution to equation (1), iteration procedure, and the data on excitation, radiation, and quenching constants are presented in [8]. For atom D, all the constants above are taken to be the same as those for H atom.

4. Results and discussion

Few examples of D_α–H_α spectral structure records are shown in figure 2 for a fixed pressure of added deuterium $p_{D_2} = 0.05\,\mathrm{mbar}$ and different pressures of added H_2O molecules. The doublet is well resolved even at a moderate dispersion of spectrometer used. One can see that if no H_2O was added, a very low intensity of H_α line exists probably due to the dissociation of residual water molecules released from the adsorbed layers on the chamber surface [12, 13]. When water molecules are added, the hydrogen line is enhanced in comparison with the deuterium line which is almost constant.

Figure 3 shows the measurement results for the concentration n_O of the oxygen atoms as a function of the concentration of water molecules injected from the outside $n^0_{H_2O}$ and n_{H_2O} in plasma at the deuterium pressure $p_{D_2} = 0.025\,\mathrm{mbar}$. Two wavelengths, 777 nm and 844 nm of an oxygen atom, were used because several research groups [14, 15] pointed out the possible interference of secondary population mechanisms of

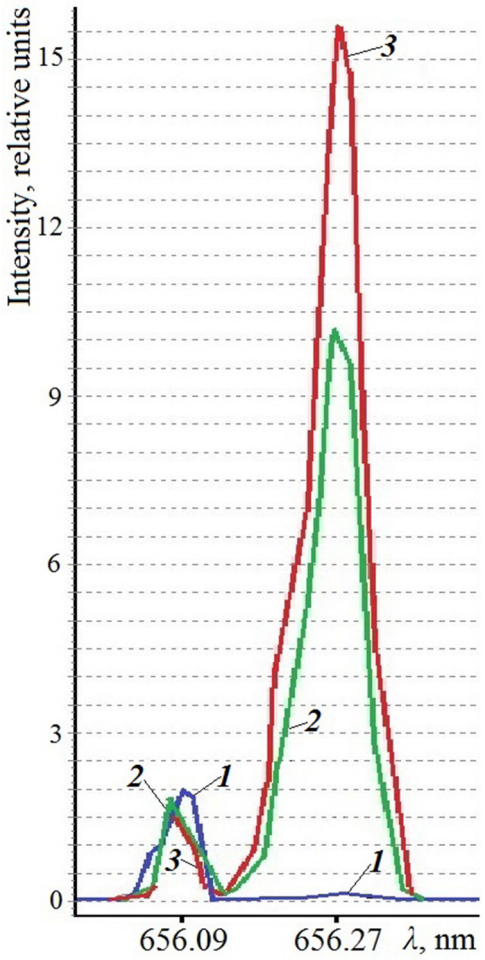

Figure 2. Spectra of a D_α-H_α doublet. Pressure of added deuterium $p_{D_2} = 0.05$ mbar. (*1*) no H_2O added; (*2*) $p_{H_2O} = 0.05$ mbar; (*3*) $p_{H_2O} = 0.1$ mbar. The both monochromator slit widths are of 0.01 mm.

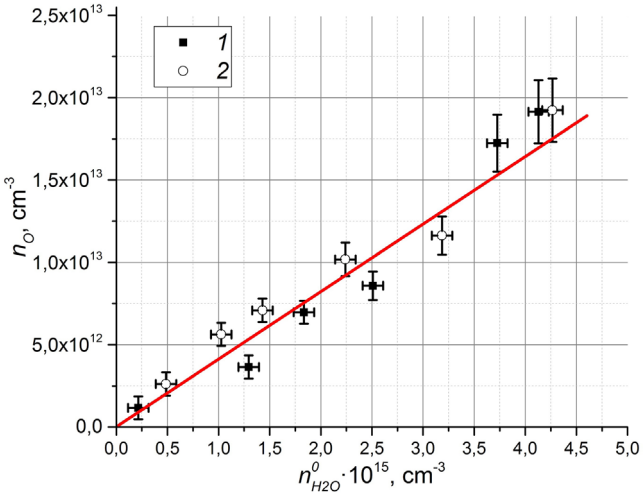

Figure 3. Concentrations of oxygen atoms measured using the lines at 777 nm (*1*) and 844 nm (*2*).

the upper, radiative state of the transition (in this case, the dissociative excitation of O_2 to O+O(3p 3P)/O(3p 5P)) in the actinometric measurement and this effect may play a higher role for the 777 nm transition than the 844 nm one. The results

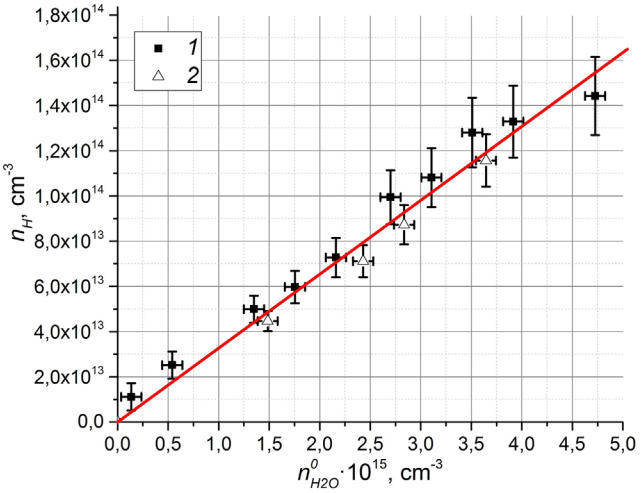

Figure 4. (*1*) initial concentration of D_2 in gas mixture $n_{D_2} = 6.75 \cdot 10^{14}\,\mathrm{cm}^{-3}$; (2) $n_{D_2} = 1.35 \cdot 10^{15}\,\mathrm{cm}^{-3}$.

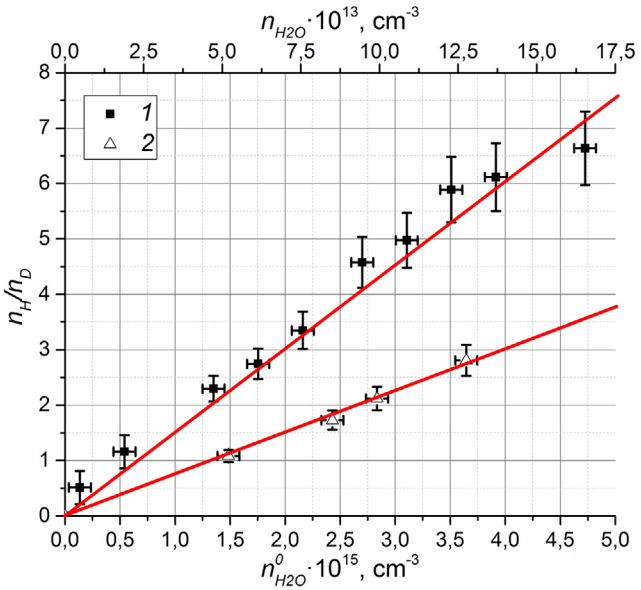

Figure 5. The n_H/n_D ratio for different amounts of deuterium. (*1*) The initial concentration of D_2 in gas mixture $n_{D_2} = 6.75 \cdot 10^{14}\,\mathrm{cm}^{-3}$; (*2*) $n_{D_2} = 1.35 \cdot 10^{15}\,\mathrm{cm}^{-3}$.

in figure 3 are close for both transitions used; thus, the dissociative mechanisms in our conditions were not revealed. The dependence n_O on $n^0_{H_2O}$ and n_{H_2O} is close to linear one $n_O/n^0_{H_2O} = \mu = (4 \pm 1) \cdot 10^{-3}$ and can be used for the actinometric measurements of the water molecules concentration.

Figure 4 presents the results of analogous measurements for the hydrogen atoms concentration as a dependence on $n^0_{H_2O}$ and n_{H_2O}. This dependence is also quite close to the linear one $n_H/n^0_{H_2O} = \gamma = 0.03 \pm 0.01$.

Figure 5 demonstrates that the dependencies of the n_H/n_D ratio on water injected from the outside $n^0_{H_2O}$ and incoming n_{H_2O} to plasma water molecules amounts for two values of $p_{D_2} = 0.025$ mbar (*1*) and 0.05 mbar (*2*) are also close to linear. The values at the upper abscissa n_{H_2O} were obtained by the method described in [8]. For measurements of water

Table 2. Measured and extrapolated sensitivities of water leaks for different pressures p_{D_2} and acquisition times 1 s and 10 s.

p_{D_2}, mbar	$5 \cdot 10^{-2}$ (measured)	$2.5 \cdot 10^{-2}$ (measured)	10^{-2} (scaling)	10^{-3} (scaling)	10^{-4} (scaling)
α, cm^{-3}	$1.4 \cdot 10^{15}$	$7 \cdot 10^{14}$	$3 \cdot 10^{14}$	$3 \cdot 10^{13}$	$1.4 \cdot 10^{12}$
Γ^0(1 s), mbar $\cdot$ $m^3 \cdot s^{-1}$	$3 \cdot 10^{-8}$	$1.4 \cdot 10^{-8}$	$6 \cdot 10^{-9}$	$6 \cdot 10^{-10}$	$6 \cdot 10^{-11}$
Γ(1 s), mbar $\cdot$ $m^3 \cdot s^{-1}$	$8 \cdot 10^{-10}$	$5 \cdot 10^{-10}$	$2 \cdot 10^{-10}$	$2 \cdot 10^{-11}$	$2 \cdot 10^{-12}$
Γ^0(10 s), mbar $\cdot$ $m^3 \cdot s^{-1}$	$3 \cdot 10^{-9}$	$1.4 \cdot 10^{-9}$	$6 \cdot 10^{-10}$	$6 \cdot 10^{-11}$	$6 \cdot 10^{-12}$
Γ(10 s), mbar $\cdot$ $m^3 \cdot s^{-1}$	$8 \cdot 10^{-11}$	$5 \cdot 10^{-11}$	$2 \cdot 10^{-11}$	$2 \cdot 10^{-12}$	$2 \cdot 10^{-13}$

concentrations in plasma, the actinometric pair 1 (see table 1) with the help of OH emission at 321 nm was used. Also one can see that the dissociation of water molecules is high $n_{H_2O}/n^0_{H_2O} = \delta = 0.035 \pm 0.005$.

Let us discuss in more detail the possibilities of water leaks monitored by n_H/n_D ratio measurements. When looking at the data in figures 4 and 5 one can write the equations

$$\gamma n^0_{H_2O} = n_H, \tag{2}$$

$$n^0_{H_2O} = \alpha \frac{n_H}{n_D} = \alpha\beta, \tag{3}$$

where $\beta = n_H/n_D$ and find the coefficient α which is dependent on n_D

$$\alpha = \frac{n_D}{\gamma}. \tag{4}$$

Equation (3) allows one to determine the concentration of water molecules initially injected into plasma from the outside by the measurements of n_H/n_D. The ratio n_H/n_D can be replaced by the ratio I_H/I_D of intensities H_α and D_α lines. This follows from equation (1) because the coefficients C, ν, A, k, Q, τ are practically the same for H and D. In some sense, the D atoms are represented as intermediate actinometric particles to measure the concentration of water-derivative particles H to obtain the concentration $n^0_{H_2O}$ with the help of relation (2).

Coming back to the motivation to measure the water leak rates by spectroscopy, we outline two circumstances.

The first is the sensitivity. The rate Γ^0 of water leak (injection) can be obtained from equation (3)

$$\Gamma^0 = \Delta(n^0_{H_2O})/\Delta t = \alpha \cdot \Delta\left(\frac{n_H}{n_D}\right)/\Delta t. \tag{5}$$

Let us estimate that the accuracy of measurements of the n_H/n_D ratio is ± 0.1. Using the above data on $\gamma = 0.03$ from figure 4, $\alpha = 7 \cdot 10^{14}$ cm^{-3} and $n_D = 7 \cdot 10^{13}$ cm^{-3} from figure 5 at $p_{D_2} = 0.025$ mbar, one can find that the observed change $\Delta(n_H/n_D) = 0.2$ in 1 s means that one can measure the minimal injection rate of water molecules from the outside as $\Gamma^0 = \Delta(n^0_{H_2O})/\Delta t = 1.4 \cdot 10^{14} cm^{-3} \cdot s^{-1}$ or $\Gamma^0 = 1.4 \cdot 10^{-8}$ mbar $\cdot$ $m^3 \cdot s^{-1}$. In the case of $p_{D_2} = 0.05$ mbar, the corresponding sensitivity is $\Gamma^0 = 2.8 \cdot 10^{-8}$ mbar $\cdot$ $m^3 \cdot s^{-1}$.

The second note is that in the majority of previous spectroscopic research [1, 2] the data has been presented with respect to the rate Γ of particles appearing in plasma due to leaks that is not the same as the rate of particle injection Γ^0 from the outside due to deep dissociation of water molecules in plasma, as previously discussed above. For example (*1*) in figure 5 $\Gamma = \Delta(n_{H_2O})/\Delta t = 5 \cdot 10^{12}$ $cm^{-3} \cdot s^{-1}$ or $\Gamma = 5 \cdot 10^{-10}$ mbar $\cdot$ $m^3 \cdot s^{-1}$.

Relations (2)–(4) and figure 5 show that when the sensitivity of the technique of I_H/I_D for leak measurements are higher, the lower the α coefficient and n_D value becomes. This is a fruitful feature for leak diagnostics in large plasma machines. Thus in the case of ITER, it is expected that the vacuum chamber walls will be processed with the auxiliary discharge in D_2 at the pressures of 10^{-3}–10^{-4} mbar [7]. Assuming that relations (3)–(5) permit the extrapolation for the wide range of p_{D_2}, one can get the following results on the leak sensitivity (table 2).

One can see that in the range of $p_{D_2} = (10^{-2}$–$10^{-4})$ mbar, the sensitivities Γ^0 and Γ satisfies the requirements of the ITER project with excess.

5. Conclusions

The possibility of using the O, H and D spectral line intensities to search and quantitatively determine the rates of water leakage into electrovacuum devices is demonstrated for the first time. These atoms can be considered as the intermediate actinometers in which densities are defined with the help of the primary actinometers Ar or Xe. The most promising seems to be the case of using the H_α and D_α spectral line intensity ratio I_H/I_D because of their very close values of excitation thresholds and emission wavelengths of D and H atoms; therefore, they represent an almost ideal actinometric pair. In this case, the parameters of plasma electrons as well as optical and electronic scheme spectral characteristics do not influence the results of measurements.

Scaling shows that this technique might be useful for wall vacuum tight diagnostics of water cooled thermonuclear reactors in 'cold' modes when the surfaces are under processing by auxiliary discharge. The possibility to use it in a 'hot' thermonuclear reactor operational mode needs additional experiments and modeling.

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