Isotopes of water molecules in a glow discharge in mixtures of helium with H₂O and D₂

A V Bernatskiy 1, I V Kochetov 1,2, V V Lagunov 1 and V N Ochkin 1

1 P.N. Lebedev Physical Institute of the Russian Academy of Sciences, Russia, 119991 Moscow, Leninskiy Prospekt, 53
2 SRC RF Troitsk Institute for Innovation and Fusion Research, Russia, 108840 Moscow, Troitsk, Pushkovykh, 12

kochet@triniti.ru

Abstract. The article presents the results of theoretical and experimental research on the concentrations of water isotopomers (H₂O, HDO, and D₂O) in plasma of a DC discharge in mixtures consisting of helium, molecular deuterium, and water vapor. Dependence of the isotopomers concentrations on the initial mixture composition is described. The measurements were performed using tunable diode laser absorption spectroscopy (TDLAS). Theoretical results were obtained with the use of a homogeneous kinetic model. The model included balance equations for charged and neutral particles and the Boltzmann equation for the electron energy distribution function in the two-term approximation. The experimental and theoretical values of H₂O and HDO concentrations were compared and showed good agreement.

1. Introduction

Water vapor admixtures in the plasma of a thermonuclear reactor, originated by desorption from the chamber surface or by penetration through the blanket wall defects, can dramatically change characteristics of plasma [1]. Determining the flow rate of water vapor and its fragments is an important task. In order to measure the concentrations of atoms and diatomic molecules, our research team has developed a few new methods of emission spectroscopy [2–5]. However, due to the special properties of polyatomic molecular spectra, the determination of their concentrations in plasma by methods remains difficult, with the exception of water molecules [3]. Studies with He+H₂O mixtures using tunable diode laser absorption spectroscopy (TDLAS) to measure H₂O concentration were carried out [6–8]. It was shown that the concentrations of water molecules directly measured by the TDLAS method fit the results of actinometrical measurements [3] and with the results of theoretical modeling well [7]. Nowadays, laser methods are actively involved in the research on processes in discharges and plasma objects [9–10].

One of the possible components of the plasma-forming gas in a thermonuclear reactor is D₂. When H₂O leaks into the chamber, it takes part in a few plasma-chemical reactions, some of which can result in the formation of HDO molecules. Formerly, we investigated the dependences of the concentrations of H₂O and HDO molecules in plasma of a DC discharge experimentally [11]. The purpose of this paper is to describe a detailed kinetic model of plasma-chemical processes in a glow discharge in a mixture, which initially consisted of He, H₂O and D₂.
2. Experiment
A fused silica tube, internal radius 1 cm, served as a DC glow discharge chamber. The length of the discharge was 45 cm. The typical voltage and current of experimental discharges were ~ (1-2) kV and 4 mA, respectively. The concentration of helium was 8.5·10^{15} \text{cm}^{-3}, the H2O molecule concentration was within the range of (4.4-9.6)·10^{14} \text{cm}^{-3}, and the D2 - (1.8-5.3)·10^{15} \text{cm}^{-3}. A detailed description of the experimental setup is given in [11]. Measurements of the concentrations of water isotopomers were made using tunable diode laser absorption spectroscopy. Following the ignition of the discharge, after the fast establishment of H2O and HDO concentrations (5-30 s), these concentrations decreased slowly. This decrease was apparently caused by heterogeneous processes on the walls of the chamber. The measurement results obtained in the early phase of discharge, (20-40) seconds after the ignition, were taken to compare the calculated and experimental data.

3. Kinetic model
The calculations were based on a spatially homogeneous kinetic model. In this model, two main parts were solved together: the Boltzmann equation in the two-term approximation for the electron energy distribution function, and the equations for chemical processes in plasma. Our model considers the following molecules: H2O, O2, H2, H2O2, HO2, D2O, HDO, D2, DO2, HD, D2O2, HDO2, OH, OD; atoms: He, O, H, D; negative ions: O\(^-\), H\(^+\), D\(^+\), OH\(^-\), OD\(^-\); positive ions: He\(^+\), H2O\(^+\), O2\(^+\), H2\(^+\), D2O\(^+\), HDO\(^+\), D2\(^+\); and electrons.

The rate constants for the processes involving molecules, atoms, and radicals and temperature dependences for those constants were taken from our previous work [5]. The model includes the processes of dissociation, ionization and dissociative attachment to the molecules O2, H2, HD, H2O, HDO, and D2O. Moreover, for H2O, HDO and D2O molecules, the processes of dissociative attachment with the formation of O\(^-\), H\(^+\), OH\(^-\), D\(^+\), OD\(^-\) ions are taken into account, respectively. For a water molecule, cross-sections for electron scattering were taken from [12]. For HDO and D2O molecules, these cross-sections were taken similarly to the H2O molecule. The set of sections for the D2 molecule was taken from [13]. Calculations showed that the processes of charged particles recombination on the walls of the chamber make a notable impact due to the low pressure of the gas mixture; therefore, the model included processes of ambipolar drift of charged particles to the walls of the chamber along with bulk recombination [14]. As shown by our previous studies [5, 8, 11], in the considered conditions, the heterogeneous interaction processes of atoms with the walls of the chamber are important. Thus, these processes were also included in the kinetic model. An equation had been added to the model for an external electrical circuit consisting of ballast resistance and a voltage source. The calculations were performed under the assumption of constant gas temperature and volume of the discharge. To solve the system of equations described above, the software package Chemical WorkBench (CWB 4.1.18411, www.kintech.ru) [15] was used. The system of equations was solved by the method of establishing the solution until plasma component concentrations in equations reach stationary values.

4. Simulation results and comparisons with experimental data
The calculations were carried out for He concentrations of 8.5·10^{15} \text{cm}^{-3}, D2 - 5.3·10^{15} \text{cm}^{-3} and H2O - 6·10^{14} \text{cm}^{-3}. The temperature of the plasma-forming gas was assumed to be constant 320 K. The discharge tube radius was 1 cm. The discharge circuit parameters for the calculation were selected under the condition of equality between the calculated discharge current for this circuit and the measured value of 4 mA.

Figure 1 demonstrates the behavior of the discharge current \(I_{\text{disch}}\) and the electric field reduced value \(E/N\) in time. The markers correspond to the strength of the reduced electric field and the experimental value of steady-state discharge current. The average value of the electron energy is 8.3 eV, and the calculated value of the established reduced electric field is 86 Td.
Figure 1. The behavior of the discharge current and the reduced electric field in time. Theoretical and experimental results are represented by solid lines and markers respectively.

Figure 2 demonstrates the evolution of concentrations of radicals and electrons over time. According to the calculations, the time of the establishment of the electron concentration is 1 µs. The radical concentrations establishment can be divided into two stages: first is around 1 ms, second is about 10 s. This happens due to the following processes: at first, the ionic composition establishes when the H₂O molecules are not yet dissociated, and the next establishment stage is due to the formation of a new neutral composition (see figure 3). Among all of the considered negative ions, the concentrations of OH⁻ and OD⁻ ions after reaching a steady-state solution are maximum. The concentrations of these ions are higher than the electron concentration by about an order of magnitude. The concentration of D⁻, O⁻, and H⁻ is about two and a half orders of magnitude lower than OD⁻ and OH⁻:

![Figure 2](image-url)
As noted in [3, 5, 7], the main process of breakdown of molecules in a discharge is dissociation by plasma electrons, and the main process of their production is heterogeneous recombination of radicals and atoms on the walls of the chamber. Unfortunately, the recombination rates are known with a small accuracy and strongly depend on the conditions of the experiment. Thus, heterogeneous recombination rates were used as fitting parameters that ensure the agreement between experimentally and theoretically obtained concentrations of H$_2$O and HDO. Three of the dependences from figure 3 are allocated in figure 4, these show the behavior of water isotopomers. Markers in figure 4 show experimental data for H$_2$O and HDO concentrations. It is shown, that by selecting the constants of heterogeneous reactions, a reasonable agreement between the theory and experiment can be obtained for these molecules at the stationary stage of the formation of the plasma chemical composition. Since the main scheme of processes includes the reactions with these molecules [5], the reliability of the behavior of other particles also should increase. But this hypothesis requires further research with new experimental data.
5. Conclusion
The homogeneous kinetic model, which describes the establishment of the concentrations of charged and neutral particles in a He-H₂O-D₂ mixture in plasma of a DC glow discharge, has been expanded. The expanded model included Boltzmann equation for the electron energy distribution function, balance equations for neutral and charged particles and the equations for the electric discharge circuit. The processes of heterogeneous recombination of particles on the walls of the chamber were taken into account. It is possible to obtain a reasonable agreement between the theory and experiment on the values of electric fields, discharge currents and steady-state concentrations of H₂O and HDO with the use of the developed model.

Acknowledgments
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