

Referee report:

Ph.D. Thesis title: "Recombination of ions in plasma at 50-300 K"

Author: Mgr. Peter Rubovič

Study programme: Physics

Study branch: Physics of Plasmas and Ionized Media

The subject investigated in the thesis is mainly devoted to the experimental studies of the recombination of atomic and molecular ions with a presence of third bodies within a relatively wide temperature range (50-300 K). The work is focused mainly on the experimental determination of the rate constants using two substantially different experimental techniques: I) Cryogenic Flowing Afterglow using Langmuir Probe (Cryo-FALP) and II) Stationary Afterglow equipped with Cavity Ring Down Spectrometer (SA-CRDS). According to the text, author significantly contributed to the construction of a new Cryo-FALP apparatus which now can achieve, unimaginable previously for this technique, 50 K. The measurements presented in the thesis, especially the observed dependencies of the recombination rate coefficients of studied ions on a reactant gas (e.g. H₂, He) or electron densities, indicate the high importance of the ternary recombination processes in plasmas. The results of the studies significantly expand our knowledge about the reactions over a wider range of temperatures.

The present work is split into 6 distinct chapters and supplemented with 8 scientific publications which are of a high standard and published in international peer-reviewed journals. The thesis is well illustrated and characterized by the logical representation of the material. The first part of the thesis very briefly summarizes the importance and the main goals of the present work. The second chapter is basically an overview of different recombination processes of ions with electrons and experimental techniques used for the studies of such reactions. The number of references in this and in the following chapters shows the ability of the author to work with the literature, to properly analyze it and to make informed conclusions. The next chapter of the dissertation is fully dedicated to H₃⁺ (D₃⁺) since the recombination process of the ion has a great importance for interstellar plasma as it initiates a chain of different ion-molecular reactions. Here, author analyzes experimental and theoretical results obtained in previous studies, helium assisted ternary recombination process of H₃⁺ is also discussed.

In the forth chapter the author is focused on the experimental set-ups used in the work. The basic principle and the configuration of SA-CRDS are discussed together with it's theory of operation. The second part of the chapter describes FALP technique, calibration procedures for the Langmuir probe, for gas velocities and for temperatures inside the flow tube. Furthermore, such important for the recombination measurements parameter as electron temperature is also taken into account and the method of its determination is explained in details.

The fifth chapter is the main part of the thesis and contains a brief description of the most important results of the author's work and completed with the attached papers. The author starts with Ar⁺ recombination process taking into account formation of Ar⁺ dominated plasma and a proper analysis of the measured data showing awareness about problems which can arise during the measurements and demonstrates the ability to think critically. Here, an excellent agreement of the measured rate coefficient of the collisional-

radiative recombination with a theory over a wide range of temperatures is obtained. In the next part of the chapter, the measurements of dissociative recombination of H_3^+ and D_3^+ ions using two previously mentioned techniques are described. The observed dependence of the recombination rate of the ions on $[He]$ or $[H_2]$ shows how presence of the third body can be significantly influential in contrast to previous knowledge about the mechanism of ternary recombination. The author also carefully analyzes and compares with theoretical predictions the results connected to the state selective measurement of H_3^+ recombination processes and finally gives an important conclusion that these ternary processes has to be taken into account in some experiments and numerical models to get valuable results. The last chapter just briefly summarizes the work.

My impression is that this work is an important step toward to more close understanding of the ion-electron recombination processes.

I would also like to put the following question:

1) In the chemical kinetic models, which are used by the author, it is usually stated that Ar gas (introduced via a reactant port) has a constant number density along the flow tube. Melting point for Argon is around 84 K. According to the results presented in the thesis the new Cryo-FALP can easily achieve temperatures below this point and in this case argon can partially be frozen near the reactant port and along the flow tube. This can lead to a longer formation time of the ions studied in the experiments due to a lower than estimated argon density and, thus, can influence the measurements of the rate coefficients at low temperatures. It would be interesting to hear the author's opinion about the possible influence of the issue on the results presented in the thesis.

Overall, the submitted thesis is original, well conducted, carefully and clearly written. The research part of the work contains high quality and innovative results. I am fully convinced that it represents significant and original contribution to the scientific field. The whole work is presented in understandable English, with some typos and errors with no influence on the scientific part of the work, and in a correct format. Author is perfectly conversant with all the details of his subject and has demonstrated high skills in the field and showed great ability to work independently and to solve professional problems. The purpose of the thesis was fully achieved at a high scientific level, which can be clearly seen from the number of publications. In the connection with the opinion expressed above, I suggest the thesis entitled "Recombination of ions in plasma at 50-300 K" to be accepted as one of the requirements for graduation of Mgr Peter Rubovič.

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