Referee report:

Ph.D. Thesis title: "Negative ion astrochemistry - a laboratory study"
Author: Mgr. Pavol Jusko
Study branch: Physics of Plasmas and Ionized Media

The present thesis is mainly devoted to the experimental studies of an interaction of negative ions (H^- and O^-) with neutral particles within a wide temperature range (10-300 K) using two different experimental setups. The work is focused not only on the experimental determination of the rate constants (using 22-pole RF trap) of the above mentioned reactions but also on measurements of the electron energy distribution of electrons produced in an associative detachment reaction of O^- anions with H_2, D_2, and CO molecules. The measurements of such distribution gives us more close to the point of understanding such reactions, as it can be easily compared with the theoretical description of the associative detachment reactions. For this purpose a novel instrument (ES-MPT) has been developed and built. According to my feeling, after reading the text, the author of the thesis has substantially contributed to the building and developing of the new set-up. The topic of this work is interesting and well motivated as such reactions are of fundamental importance in understanding and accurate modeling processes related to astrochemistry.

The thesis is split into 6 chapters. In the first part the author very briefly summarizes the importance and the motivation of the present work. The second part is the theoretical description of the motion of charged particles at different conditions: (a) in homogeneous a magnetic field which is relevant to the magnetic mirror traps (b) in static and rf electric fields for clear understanding effects of various parameters in multipole traps (e.g. voltage amplitude of the applied rf signal and the static voltage difference between the the rods). Here, the author provides a detailed description, mathematical formulation and solution of the problems, characterizes and understands properly its complexity.

The third chapter is focused mainly on the main components of the experimental set-ups applied in this work. Here author describes the Storage Ion Source used for the charged particle production. The chapter contains a brief overview of the particle detection system, and it also shows awareness about problems which can arise during the detection, such as possible influence of the magnetic field, etc. H atom source is additionally mentioned with its theory of operation. The atomic beam velocity distribution and beam density in the trap were carefully determined. The second part of the chapter author devoted to the proper determination of the reaction temperature which is a crucial parameter for such measurements.

In the next chapter, associative detachment reactions using the rf ion 22-pole trap are studied over a wide temperature range. This part of the thesis is started with an overview of the importance of such reactions and, as a consequence, experimental determination of the rate coefficients especially at very low temperatures. The measured data for the associative reaction of H^- with H were compared with theoretical calculations and some previous measurements and showed a good agreement. The reactions of O^- with H_2 (D_2) were also studied before but only for 300K. The present work gives significant contribution to expand the knowledge about the reaction over a wider range of temperatures (10-300K). The data at higher temperatures are compared with previous measurements and the isotope effect is briefly discussed. Here, the author also pointed out about the possibility of the formation of triatomic anions such as H_3^- and D_3^- in the trap and estimated the upper limit for the ternary association reaction of $H^-(D^-)$ with H_2 (D_2)

The fifth chapter deals with the measurements of the electron spectra of the associative detachment reaction of the ions stored in the trap. Such experiments can provide great insight into understanding of the reactions. For this purpose, the novel experimental set-up has been developed and built. The instrument is basically a combination of an electron spectrometer and the rf ion trap. The spectrometer part was built (according to the author) completely from the beginning. Author in details describes the experimental set-up (original solutions with combination of the diagnostics methods), its theory of operation, calibration procedures. Finally author provides first experimental results on investigation of the associative detachment of O^- with H_2, D_2 and CO molecules. The rate coefficient measurements of such reactions based on using the electron flux (counting electrons) were compared with the results of the previous experiments. Furthermore, the fist measured electron energy distributions are also presented. The data shows a good agreement between theoretically calculated and the measured spectra. Author carefully analyzes the results and gives an important conclusion that molecules produced by such reaction are highly internally exited and the energy stored in the kinetic energy of electron is considerably small. In the final part of the chapter, the possible further improvement of the set-up is discussed.

In the last chapter the author shortly summarizes the work. The thesis is supplemented by 2 scientific publications in international peer-reviewed journals in which, to my opinion, the contribution of the author was significant.

I would also like to ask the following question:

On page 42, it is stated: "We are certain that the eventual condensation of the neutral gas on the 22 - pt wall are not significant." It would be interesting to know, what this conclusion is based on, since author does not say it explicitly in the text. One can assume that the sticking coefficient of H_2 (D_2) molecules on the cold trap surface, especially at very low temperatures, can be quite high. In this case, if the effect is not taken into account, it can lead to the overestimation of the H_2 (D_2) number density inside the trap and, as a consequence, to the underestimation of the measured rate coefficient. Could the author, just briefly, comment on this possible problem?

In summary, the submitted work is written carefully, transparently and technically correct. The research presented in the thesis quite complex, innovative, and contains high quality and original results. The work is written in understandable English, with only a few typos and errors which have no influence on the evaluation of the work. The author has demonstrated extensive knowledge and high skills in the field; he critically evaluated the experimental data and showed ability to work independently. The purpose of the thesis was achieved fully and at a high scientific level. Based on the opinion expressed above, I suggest the thesis entitled "Negative ion astrochemistry - a laboratory study" to be accepted as one of the requirements for graduation of Mgr Pavol Jusko.

19.07.2013 Budapest

Mgr. Ihor Korolov, PhD