

June 14, 2019, Prague

Referee report for evaluation of doctoral thesis:

Mgr. Ábel Kálosi: “Elementary Processes at Low Temperatures – Reactions of H_3^+ and N_2H^+ in Afterglow Plasmas”

The doctoral thesis of Mgr. Ábel Kálosi concerns several experiments related to dissociative recombination of small molecular ions in cold, astrochemical related environments. The experimental work was carried out under the supervision of doc. Radek Plašil in the laboratory of prof. J. Glosík, where experiments in afterglow plasmas and spectroscopy of such ions have long tradition. The group has contributed to the understanding of the chemistry of early universe, especially for recombination processes of H_3^+ ion. The thesis of Á. Kálosi brings the work of the group further and can be divided into several main topics:

1. The construction and the commissioning of a new cryogenic stationary afterglow apparatus equipped with CRDS working in the temperature range of 30-60 K.
2. Low temperature measurements with H_3^+ ions and its deuterated isotopologues (H_2D^+ and D_2H^+) with the aim of determining the correct neutral gas and ion translational temperatures and the relative ion densities.
3. Precise absorption spectroscopy of N_2H^+ ion.
4. The development of the data processing algorithms for CRDS measurements (and corresponding plasma modelling) and revision of older experimental data.

The work is divided into 10 chapters. The chapters are written in the order in which they were executed. As this does not always mean the chronological order, such arrangement makes orientation bit harder and it is sometimes confusing. The thesis is written in a relatively good English, there are only very few mistakes and typos. The results are well documented in figures, however the text is often very lengthy and dense and it would be beneficial to include more figures, which would make the reading and finding the right information easier. Also, figures containing some of the key results (for example Figure 16) are very small and should be much

larger for correct interpretation. The literature survey used in the work is very well documented with plenty of references, including also the work of the group. Overall, I appreciate the high formal standard of the thesis. The author also includes his own contribution at the beginning of each chapter containing results and often refers to the other work published by the former and present members of the group.

The thesis is accompanied by two papers published in well established and impacted journals (Journal of Instrumentations; Review of Scientific Instruments), which are included as an attachment. Á. Kálosi is the main author of one of them. Their scientific quality has been verified in a peer review process, so I do not add any comments on them.

Major comments and/or questions:

1. Reinterpretation of the published data and additional comments of the author gives the reader eventual feeling that the previously published results are not up to date. Are the published results preliminary? Why has the author not used the possibility of sending errata to the original papers?
2. There is too much space devoted to merged beam experiment (particularly Cryogenic Storage Ring in MPIK Heidelberg) but there are neither any results presented from this experiment nor any details of the author's contribution to this experiment. Therefore, I consider inclusion of this part to be redundant.
3. Larger part of the work is dedicated to the data processing of CRDS data. I miss the information about the tools used for the data processing (i.e. programming/script language) and used libraries. The SciPy library is mentioned in the text, so I assume that Python scripting language was used. Is this information correct? I also miss inclusion of the code in the attachment of the thesis, as it should be its integral part.
4. What are the operational temperatures of the cryogenic SA CRDS apparatus connected to the first stage of the closed cryostat? Has any strong freezing of the gasses on the walls of the apparatus been observed? Would it affect the forming of the desired ions or their thermalization?
5. Given the length of the author's doctoral study I can see that more than two papers were published with his authorship (according to the Web of Science, 7 papers were submitted and 8 were published). Why are not all the author's papers published during his study included in the thesis?

In summary, the thesis demonstrates the author's ability to perform independent scientific



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work. In spite of the abovementioned comments, I recommend the presented thesis for the defence, and the author to be awarded the Ph.D. title after a successful defence.

RNDr. Peter Rubovič, Ph.D.