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Referee report for evaluation of PhD thesis: Mgr. Peter Rubovič: "Recombination of ions in plasma at 50-300 K"

The thesis of Mgr. Peter Rubovič concern several experiments performed in the group of Prof. J. Glosík investigating recombination reactions of ions. During the recent couple of years I have had the privilege to referee several theses from this group, and I became used to their relatively high standard. The present work of P. Rubovič is by no means an exception from this "rule". It nicely summarizes a complex work which was done on several experimental apparatuses built in the group, and represents a comprehensive overview of the recent activities in the field of recombination (namely of the H<sub>3</sub><sup>+</sup> ion).

The topic of the thesis –which is essentially the recombination of  $H_3^+$  ( $D_3^+$ ) and  $Ar^+$ - might seem relatively limited. However, the author nicely demonstrates the complexity of these relatively simple systems. The  $H_3^+$  recombination has been studied for more than 60 years, and despite its simplicity (the system involves only 3 nuclei and 3 electrons –if the influence of "third bodies" is not involved) it is not yet understood completely, as demonstrated in the thesis. The thesis also shows the substantial –or rather world-leading- contribution of the present group to the study of this problem. In addition, the different experimental approaches and dedicated experimental setups are nicely introduced in the thesis.

It should be also stressed that the interest in the  $H_3^+$  recombination reaction is not purely fundamental, but represents an important topic in the chemistry of interstellar medium. Therefore I evaluate the present thesis as topical and providing the leading results for the given topic of  $H_3^+$  recombination.

The thesis is also written in relatively good English, and I was able to find only a few typos and errors. The arguments are well formulated and understandable. I also appreciated the high standard of the thesis form including the graphics.

The thesis is based on 8 articles published in (highly) impacted international journals, which are attached as a part of the thesis. Their quality has been, indeed, assessed in a stringent peer review process, and therefore I am not commenting on them.

There are several questions which I would like to ask the author in the defence process:

In many places the nuclear spin temperature in discussed (e.g., page 15, 27, etc.). It is well defined by thermal equilibrium within one manifold of energy levels —ortho and para. In collision-less system these two manifolds are independent, since the ortho $\leftrightarrow$ para exchange requires a nuclear spin flip which is only possible in highly non-homogeneous magnetic fields. The equilibrium between ortho and para manifolds can be established by collisions: either surface collisions causing the spin-flip; or gas phase collisions where hydrogens with different spins can be exchanged between  $H_3^+$  and  $H_2$ . These exchange collisions have certain

"selection rules" which may prevent the system from reaching the ortho-para equilibrium if the collisions are infrequent. In the view of this discussion it might be interesting to evaluate NS temperature within each manifold separately rather than using eq. (35) and (36) assuming the ortho-para equilibrium. How do these temperatures differ from the currently defined  $T_{NS}$ ? I would also welcome some discussion on the concept of temperature in non-equilibrated systems—this concerns especially the storage rings.

I usually try to avoid the standard question about the authors' actual contribution to the evaluated work. However, the present thesis provides a really nice and valuable overview of the recent few-years' activity in Glosiks' group in the field of  ${\rm H_3}^+$  recombination. The author combines results of several experiments and often refers to other recent thesis from the group. Therefore, I would like to hear his own assessment of his own personal contribution to all these complex results –I have no doubts that it was, indeed, substantial.

In summary, the present thesis demonstrates the authors ability to perform independent scientific work. Therefore I recommend the present thesis for the defence, and the author to be awarded the Ph.D. title after a successful defence.

Michal Fárník

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