Referee Report:

Ph.D. Thesis: **"Recombination and Reactions of Ions at Thermal Energies"**

Author: **Mgr. Ihor Korolov**

The subject studied in this thesis is mainly the recombination of various molecular ions in Flowing Afterglow (FA) plasmas. The author has probably substantially contributed to the building of a new FA-Lagmuir Probe apparatus (FALP), which is described in the first part of the thesis. Also the data acquisition and data analysis procedures are described in some detail. Especially a new method of evaluation of the Lagmuir probe measurements is introduced to derive reliable Electron Energy Distribution Function (EEDF) in the FA plasmas, which in turn can be used to obtain the recombination coefficients.

In the second part of the thesis the recombination studies of various molecular ions in FA are studied. First H_3^+ and D_3^+ ions are mentioned. Since these are probably the most important results of the present work, they are discussed in a great detail, considering various possible dependencies of the measured recombination rates. Regarding the importance of these recombination rates for interstellar plasma as well as for various terrestrial plasmas, and at the same time the ambiguity of the recombination rates obtained in various experiments and theoretical calculations over the past more than 30 years, the *new results* presented here are *very important*. Especially, the observed dependencies on the reactant (H_2, D_2) and carrier gas (He) number densities indicated importance of the ternary recombination processes in plasmas. On the other hand, the binary recombination rates after subtracting the higher pressure effects are in a good agreement with the single collision experiments and the theory. This is an important *novelty* of the present work . Along the same lines, also the consideration of H_3* and D_3* Rydberg metastable molecules in the plasma models is a new important feature, as well as the discussion of the possible *ortho-* and *para*-H_3^+ role in the recombination.

Further, the recombination of KrH^+, KrD^+, XeH^+, and XeD^+ is studied. Studies of these species are more of a fundamental interest for the sake of a precise theoretical analysis. Finally, recombination of molecular ions HCO^+ and DCO^+ is discussed. These species and their processes potentially play a key role in the interstellar gas clouds. Therefore their studies are well justified and *quite topical.*

In summary, the thesis contains some highly topical results. The implemented experimental method has been developed into an very high degree of accuracy by the author with inclusion of most possible effects, which could influence the results. It points to a very *diligent work.* Formally, the work is mostly written in a clear understandable English, with only a few typos and errors. The thesis is accompanied by 8 scientific publications already published or submitted for publications in mostly international reviewed journals, some of them quite highly ranked (*Phys. Rev. Lett.*). To my mind, according to the text of the thesis the contribution of the author has been substantial to at least 6 of these publications, which is a very high standard.

I would like to rise 2 questions:

Q1: On pg. 79 the author mentioned that the recombination of HeH^+, NeH^+, and ArH^+ has been measured in storage ring experiments. The KrH^+ and XeH^+ ions are too heavy for such studies, therefore they are

investigated in the present FALP experiment. However, would not it be wise to study also some of the above mentioned lighter ions in the FALP experiment, to see, how the FALP value compares to the storage ring one? Indeed, according to the H_3^+ studies FALP seems to be now giving results quite in agreement with the storage ring values -or at least, the differences now seem to be quite understood- however, other sources of discrepancies might occur for the RgH^+ types of ions.

Q2: On pg. 71 the author claims that the *ortho-* and *para*-H_3^+ ions are in equilibrium via the reaction (3.10) of these species with H_2 molecules, which proceeds in both directions with approximately the same rates. I do not quite see the argument, based on the reference given in the work. One should also consider reactions with *ortho-* and *para*-H_2 molecules, or are these somehow considered implicitly? Indeed, the various *ortho* and *para* species posses different energetics, which may lead to different rate constant, especially at low temperatures, but this is probably not of concern at the high plasma temperatures considered here. Could the author briefly comment on this issue?

All, what has been said above documents the undoubtedly high qualification of the author, his ability to work independently: built a new experiments, develop new methods for data analysis, critically evaluate the experimental data and formulate sound scientific ideas and conclusions about the studied processes. Therefore I suggest the present work to be accepted as one of the requirements for graduation of Mgr. Ihor Korolov.

2.6. 2008 in Prague

Michal Fárník