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Stockholm, 2023-04-14

### **To whom it may concern**

#### **Review of the habilitatiin thesis of Petr Dohnal, Charles University Prague, CZ**

The thesis mainly focusing on the recombination of atomic and molecular ions with electrons. This is a very important process in the interstellar medium and planetary atmospheres, but also a decisive role in man-made plasmas like those encountered in combustion engines and nuclear fusion reactors. Special attention is devoted to the role of assistance by third bodies to the recombination process, an area where the team in Prague has gained considerable experience and made many important contributions. This subject is often a bit neglected by astrochemists since three-body processes generally play a minor role in the interstellar medium. Also, the influence of different rotational quantum states on the recombination process has been investigated by the applicant, a subject that has gained increased attention in the scientific community during the last decades.

The presented experiments were performed using various modifications of stationary afterglow (SA-CRDS, Cryo-SA-CRDS) and flowing afterglow methods using Langmuir probe (Cryo-FALP II). The Prague group has long-standing experience with this technique and are one of the leading groups in the world applying them. Nevertheless, the author has introduced some important innovations that contribute to the originality of the thesis. He as also been involved in experiments employing ion traps which broadens his research expertise. Neverthelees, those studies play a more minor role in the present thesis.

In the first chapter the author gives a brief overview about the different recombination processes and the usual rate coefficients encountered with them. The theoretical background of these reactions is outlined and the relevant mechanisms are discussed. The second chapter concerns the methodology applied, herein the different methods are described. This includes the Flowing-afterglow Langmuir Probe (FALP) method and the Stationary afterglow with Cavity Ring-Down spectrometer (SA-CSDR). In these descriptions the applicant shows fundamental understanding of the different methods and has also designed a microwave source. The following chapter is devoted to an overview of the data analysis in which the data analysis in the study of different recombination scenarios are outlined. The validity of the data analyses for those scenarios have been tested using different reactions as benchmarks.

The subsequent chapters describe the results of the studies. The first system tackled is the reaction of  $\text{H}_3^+$  with electrons. The rate constant of this reaction at low temperatures has been a matter of intensive debate in the scientific community and the team at Prague has contributed with some very important studies on this matter. The disagreements were mainly due to the role of third bodies in this process. Since the dissociative recombination of  $\text{H}_3^+$  ions is of paramount importance in the interstellar medium, exact knowledge of its rate constant is absolutely necessary. The applicant used improvements in instrumentation to verify that the rotational and nuclear spin state populations of the recombining ions are in accordance with thermal equilibrium with the buffer gas. He and his co-workers also obtained the binary recombination rate coefficients of para and ortho  $\text{H}_3^+$  ion. Results were in excellent agreement with theoretical predictions. This is a major success probably putting an end to discussions in the scientific community going on for several decades.

The studies were then extended to deuterated isotopomers of the  $\text{H}_3^+$  ion detected in the interstellar medium, namely  $\text{H}_2\text{D}^+$ ,  $\text{HD}_2^+$  and  $\text{D}_3^+$ . It was the first time a detailed study of the dissociative recombination of this species was undertaken using flowing afterglow methods.

Another reaction studied was the dissociative recombination of  $\text{N}_2\text{H}^+$ , a very important interstellar ion whose abundance is also used as a diagnostic tool in many astronomic objects. Very good agreement was found with previous storage ring experiments at higher temperatures, whereas at low temperatures there was a disagreement noted at low temperatures, which was ascribed to different populations of rotational states in the two studies, which is a reasonable explanation.

Also, the dependence of the dissociative recombination rate constant of  $\text{N}_2^+$  on the vibrational excitation of the ions was studied. This value has been the subject of intense discussion during the last decades and is of great importance in nitrogen-dominated planetary and satellite atmospheres. By using simultaneous measurement of time evolutions of  $\text{N}_2^+$  and electron number densities the applicant was able to exactly determine the recombination rate coefficients for  $\text{N}_2^+$ . Such studies are experimentally very challenging and time consuming but of great relevance.

In the present thesis the author also reported some studies using ion traps in which he was involved. For the  $\text{OH}^-$  ion he and his co-workers not only succeeded to determine the rotational temperature of trapped ions but also to pinpoint the rotational state populations of the probe ions and to establish that these values point to a thermal equilibrium over a wide temperature range. Another ion trap study concerned the  $\text{HCN}^+$  and  $\text{CN}^+$  ions with  $\text{H}_2$ . With those investigations the applicant has clearly shown that he is capable to use many different methods in his studies. However, since he was not the main investigator in the ion trap studies, the discussion of these experiments is rather brief in the thesis.

The choice of the systems to study and to be included in the thesis was very well motivated. In several cases long-lasting disputes about the recombination rate coefficient of ions of pivotal astrochemical importance could be resolved. The research presented in this thesis is therefore highly relevant and state-of-the-art. The author was also engaged in several improvements of the experimental devices in Prague. The Cryo-SA-CRDS apparatus was upgraded to enable operation in the temperature range of 30 – 300 K.

The thesis is very well written and easy to follow for a scientific reader. The use of the language is very good, only in some few cases the choice of uses of articles or not (a difficult thing in

English especially for speakers of languages in which articles do not exist) could be improved. Only very few typos exist in the manuscript. The figures are very instructive and their layout is nice.

The choice of the attached journal article shows that the applicant is publishing in leading international journals. Regarding the Turnitin plagiarism analysis the high matching grade of 48% at first seems surprising. However, this is partly due to the fact that the thesis consists to a large extent to attached publications. The largest matching (22 %) is found with the Ph. D. thesis of the applicants. Inspection of the analysis of the matched text parts, however, shows that these matches quite often consist of generic clauses and standard text fragments which are fairly uncritical for the quality and originality of the work. Quite often, also literature citations are flagged as plagiarism, which is definitely a shortcoming of the programme. Further matches apart from with the applicants the thesis are in the single-digit percentage and concern mostly papers produced by the author of the habilitation thesis. Therefore, there is no indication of considerable and systematic plagiarism in the thesis that would challenge its validity and originality.

Overall, the thesis is of very high scientific quality and very well laid out. Thus, therefore I strongly and without any hesitation I ask the relevant bodies to endorse the relevant bodies to accept the thesis.

Yours sincerely,

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