

## Ph.D. Thesis Evaluation Report

Author: Artem Kovalenko  
Title: Laboratory studies of reactions of  $O^+$  and  $N^+$  ions with molecular hydrogen and its isotopologues, HD and  $D_2$ , at low temperatures.  
Reviewer: Mgr. Viktoriya Poterya, Ph.D.

The thesis describes the major results which were obtained during PhD studies and it focuses on the chemical kinetics of ion-molecular reactions between ions  $O^+$  and  $N^+$  and neutral molecular hydrogen together with its isotopologues. The studied reactions are the key processes in the interstellar medium. The investigation of the rate of these reactions, the effect of the Temperature, Collision and Activation energy is especially important due to vast variation of interstellar conditions ranging from ultra-cold molecular clouds environments to hot ionized medium. The reactions with deuterated species are important to understand the isotopic partition, moreover they contribute to develop new theoretical methods for aspects of collision dynamics.

The thesis is composed of four chapters.

In the Introduction author describes the current stage of research of ion-molecular reactions which are important in the interstellar space. The terms of molecular kinetics including the rate constants of reactions are described in the subsection. The last part of Introduction is devoted to the measuring techniques which were used to study ion-molecular reactions and reactions cross sections.

In the second chapter the goals of the thesis are outlined.

In the third chapter author describes the experimental methods together with experimental setup which was used to carry out the experiments during Ph.D. study.

The last chapter presents the results of the research conducted during the Ph.D. study. In the subsection 5.1 the kinetic of the reaction of  $O^+$  ion with  $H_2$  is analyzed. The special attention was paid to choose the proper ionization condition in order to produce the  $O^+$  ion in the ground electronic state and reduce the error in the rate of reaction due to state specific reaction. The dependence of the reaction rate on the  $H_2$  number density indicated that reaction is bimolecular. The temperature dependent coefficients of reactions were determined. It is an important finding which can be used for the modelling of the reaction kinetic relevant to the different areas in the interstellar space. The investigation of the reaction  $N^+$  with HD and  $D_2$  resulted in measurement of the important parameters such as rates of reactions and calculation of activation energies. The studies of  $O^+$  reactions with deuterated molecules provided the values of rate coefficients for broad temperature range and also the value of ratio for  $OH^+$  formation versus  $OD^+$ .

The thesis is scientifically sound. The goals of the thesis are clearly defined and the content of the thesis meets the set goals. Determination of the absolute values of parameters of reactions kinetics require the precise calibration of the experimental methods and thorough examination of each measurement step. Author clearly explain the parts of the experimental setup together with the details of the measurements and data analysis. In general, the work is easy to read. A slight difference in perception exists however between the different chapters. In the Chapter 5, I suppose that the author, in order to avoid similarities and repetitions, tried to present the text in his own way. However, since the English is not the author's mother language, some parts of the text are perceived ambiguously. But there are very few such cases. Concerning the results of the programs for the plagiarism, I didn't notice the whole sentences with complete similarities. Additionally, in scientific writing it is difficult to avoid cross-match, since academic terms and names practically impossible to replace by synonyms. The writer should possess the extensive experience in writing in order to produce not only scientifically valid articles but also literary masterpieces.

I suggest some grammar and content corrections.

## Suggested revisions

### Grammar:

- p. 23 "secular motion" shouldn't be circular?
- p. 27 the words combination "my work" sounds too much personal, I suggest this work, but I have to admit that here I'm not sure about the rules for thesis writing.
- p. 48 last paragraph "penetrate the ion trap..." add into the ion trap.
- p. 51 first paragraph "it is described" replaced by it will be described.
- p. 52 "compere" replace by compare.
- p. 61 last paragraph "groped" should be group and experimental methods can be replaced by experimental techniques.
- p. 64 first paragraph word "align" I would replace by level off since the meaning of what actually happens with data becomes confusing. I also suggest to replace this word in other places of the manuscript.

### Content:

- Author mentions that data were fitted using kinetic models. It would be desirable for clarity at least ones mention what kind of software was used to model the kinetics.
- p. 58 last paragraph in sentence "The first data point represents the situation when ions do not have enough time to cool down ..." it has to be specified which data points author describes.
- p. 69 "It indicates that the relaxation of  $N^+$  ions does not have an influence ...." it has to be clarified what is meant by word relaxation in this particular case.

## Summary

The experiments were carried out using complex experimental apparatus. In order to measure the rates of reactions at low collision energies and obtain the parameters of the reaction kinetics the complementary experiments are often needed for calibration and system testing. Author showed that he successfully learned experimental methods which were applied to investigate the ion-molecular reactions. The obtained results are novel and they can greatly contribute to description and also modelling the interstellar chemistry. The novelty of the results is confirmed by their publication in the impacted scientific journals.

Author demonstrated an ability for independent work. Thesis fully satisfies the requirement for obtaining a PhD degree.

I recommend the PhD thesis of Artem Kovalenko, entitled "Laboratory studies of reactions of  $O^+$  and  $N^+$  ions with molecular hydrogen and its isotopologues,  $HD$  and  $D_2$ , at low temperatures" for the defense.

## Questions on author

1. Technical question: why the RF electrodes in SIS has this specific shape?
2. The rate of reaction of  $O^+$  with  $H_2$  and  $OH^+$  formation  $k$  was determined with the precision of  $(1.3 \pm 0.5) \times 10^{-9} \text{ cm}^3\text{s}^{-1}$ , what is the major contribution to the error factor of  $\pm 0.5$ ?
3. It is interesting that  $k$  for  $NH^+$  channel formation and  $k$  for reaction with  $D_2$  and  $ND^+$  formation has similar dependence on  $T$  while the rate coefficient of the  $ND^+$  formation in reaction with  $HD$  shows the negative temperature dependence at  $T$  above 200 K. What is the reason for such dependence? Can it be connected with much lower  $E_a$  which was found for this reaction?
4. Somehow, I missed in the text if the branching ratio for  $NH^+$  formation in  $N^+$  reaction with  $HD$  was measured. If it was obtained, can it be compared to the  $OH^+$  branching ratio?

19.02.2021

Opponent

Mgr. Viktoriya Poterya, Ph.D.