Ph.D. Dissertation thesis report

Author: Dmytro Shapko
Title: *Experimental study of the dissociative recombination of molecular ions at temperatures relevant to cold interstellar plasma (30-300 k)*.
Reviewer: Mgr. Viktorie Potery, Ph.D.

The Ph.D. thesis is entitled "Experimental study of the dissociative recombination of molecular ions at temperatures relevant to cold interstellar plasma". The thesis follows the classical structure and thus contains main chapters such as Introduction entitled Theory, Experiment, Results and Discussion, Conclusion. Bibliographic sources are properly cited. The thesis refers to 7 published articles which are attached in a separate document.

The objectives of the thesis reflect the current scientific developments in the field of astrophysics. Rate constants for ion-molecule reactions with electrons are crucial for modelling the chemical composition of numerous interstellar regions. The recombination decay processes, as outlined in the theoretical part of the work, can depend strongly on the collision energy, but also on the internal states of the reactant. Differences in the measured recombination rates of the fundamental interstellar ions, H_3^+ and N_2H^+, determined under different laboratory conditions, can be considered as a consequence of this fact. Quantification of the decay rate as a function of temperature and the internal states of the recombining ion is therefore particularly important.

The experimental apparatus has been described in detail with emphasis on performing electron density measurements by monitoring the resonator frequency. Schematics of the electronic configurations are shown and explained in detail.

The results section includes two main research projects: measurements of N_2H^+ recombination in the temperature range 85 -350 K and investigation of recombination of H_3^+ ions in the buffer gases He and Ne. In the case of N_2H^+ recombination, the internal rotational and vibrational temperatures have been determined to accurately define the quantum states of the recombining ions. The determination of the recombination rate in the low temperature region was also an important finding. No change in the recombination rate was observed under elevated pressures of the buffer gases, He and H_2.

The complementary microwave diagnostic method for measuring electron number density in Stationary Afterglow apparatus with Cavity Ring-Down Spectrometer was used to investigate H_3^+ recombination at a low temperature of 110 K in Ne gas. The results showed that the simultaneous independent determination of electron and H_3^+ number densities allows the recombination rate of the ion of interest to be calculated even under conditions where another positive ion contribute to the electron loss.

The conclusion section is written in a clear manner.

The formal structure is logical and proportional and contains all the necessary components. Perhaps in some parts the style was not scientific but rather narrative, but on the other hand it shows an independent elaboration by the author. Regarding the issue of plagiarism, the evaluation software showed a low level of similarity.

Summary

Ph.D. candidate has conducted thorough and comprehensive research.
The results obtained have great potential for use in astrochemical models to predict the abundance of nitrogen-containing species and to characterize the composition of low-temperature regions of interstellar space. The novelty of the results is confirmed by their publication in peer-reviewed journals.
Author demonstrated an ability for independent work.
Thesis fully satisfies the requirement for obtaining a Ph.D. degree.
I recommend the Ph.D. thesis of Mgr. Dmytro Shapko, entitled "Experimental study of the dissociative recombination of molecular ions at temperatures relevant to cold interstellar plasma" for the defense.

Suggested revisions/corrections.

Page 28, second paragraph from the bottom, "estimate the production of NH_3", it is not clear how NH_3 can be produced, maybe some words should be added.

Page 53, last paragraph "vibration temperature", should be vibrational.

Page 59, second paragraph "we take in to account", should be into.

Page 61, "Similar experimental researches were" maybe just experiments.

Page 84, the sentence "But what is more important in the present case, is that the equality of the measured recombination rate coefficients was observed even for the experimental conditions where the number densities of electron and H3+ ions and, as a result, the curves diverge greatly on the graph", this sentence has to be corrected, some words are missing.

Questions on author.

1. The quantum states of the recombining N_2H^+ ions are quite important parameters knowledge of which helps to eliminate the errors in determining the recombination rate. Figure 10 shows the fractions of observed rotational states, can you please say more about how they were measured and how further calculations were performed?
2. Concerning the N_2H^+ ion probed in the first vibrational state, what is the lifetime of this excitation? I was wondering if the collisions with He cannot quench the vibrational excitation especially in the experiments where the dependence on He concentration was measured. Was it somehow also considered? There is a quite informative article where vibrational quenching in neutral collisions is investigated (E.E. Ferguson, J. Phys. Chem. 90 (1986) 731).
3. In the kinetic model, NH_3 impurities was added as an important reactant. What was the source of this impurity in the experiment? Water was not considered in the model, how did you ensure that traces of water would not interfere with your experiments?
4. Since in the introduction you focused on the theory of dissociative recombination and laboratory studies of recombination rates, I was wondering if you could talk a bit about the current state of astronomical observations of H_3^+ and future astrophysical prospects of H_3^+. The H_5^+ is also a critical ion and even more complex hydrogen ions have been observed, have you considered measuring H_5^+ recombination, especially focusing on different internal states.

15.08.2023

Opponent Mgr. Viktorie Potery, Ph.D.