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To
Prof. RNDr. Zdeněk Doležal, Dr.
Vice-Dean for Research and International Affairs
Charles University
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Report for the Habilitation thesis of Petr Dohnal
"State Selectivity in Recombination of Molecular Ions with Electrons"

With great interest I read the habilitation work of Dr. Petr Dohnal for which you asked me to prepare a report which I am delighted to do herewith. Before going into details, I am impressed by the work of Dr. Dohnal and I strongly recommend to accept his thesis as part of his habilitation.

I follow the work of the working group led by Prof. Juraj Glosik ever since my time as an assistant in the group of Prof. Gerlich in Chemnitz in the mid 1990s, i.e. for more than 20 years. There is a common interest in plasma physics, especially in low temperature and low-density plasma processes which play a significant role in astrochemistry. We share a great interest in the key molecule H_3^+ and its deuterated siblings but also many molecular ions which are related to this central proton donor in space environments. The specialty of my research group concerns the spectroscopy of molecules present in space and since we developed or co-developed a number of crucial techniques for ion spectroscopy there is also some significant overlap in this direction to the work of Petr Dohnal.

The thesis of Dr. Petr Dohnal concentrates on the work related to “Recombination of Molecular Ions with Electrons”, a subject we are not dealing with in my research group but which is of utmost importance for the abundance of many ions and also neutral molecules in space. Because of this complementarity of our research I read the thesis with very great interest and I learned many details as the thesis is a comprehensive report of the state-of-the-art in this field.

The thesis starts with the theoretical background required to understand the work presented in the thesis. This background is laid out in a few pages but

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prepares the reader in what will follow. Another chapter is added reporting on absorption spectroscopy in general and Cavity Ring-Down Spectroscopy (CRDS) in particular because spectroscopy is an important ingredient and new tool to investigate the “Recombination of Molecular Ions with Electrons” in particular if this study should be state-selective as desired by the author.

Following these descriptions Petr Dohnal describes other fundamental techniques, Langmuir probe diagnostics and Microwave diagnostics, which are essential to understand the working principles and the measurements discussed in the result section and of course in the 18 attached original works.

— The experimental setups which were either build and/or significantly improved by the author are described next. With building the Cryo-FALP II setup and the Stationary afterglow with Cavity Ring-Down spectrometer Petr Dohnal establishes himself as a mature scientist in the scientific community. With his instruments he is able to conduct research which is not available in any other laboratory. These instruments are consequent further developments of technologies which are well established for sometimes more than 50 years but with the combination of spectroscopy, which addresses specific molecules and in the best case, even specific internal states of those, the field is advanced in a very fundamental way.

— It is very good to see how these advancements are based on the long-time experience of the group, which creates the international reputation of the Prague institute, now puts the whole field an important steps forward because new details are discovered which were hidden in previous work. In this way Petr Dohnal creates his unique place in the international community.

In the results section the author summarizes the main results of his work which is laid out in great detail in the attached original works. This work is very impressive in its detail but also in its breadth. As mentioned above H_3^+ and its deuterated siblings play a significant role in this work. What is very special about the techniques is the fact that the influence of ternary processes can be studied in detail. This is done for a number of examples and it is very interesting to see how this is compared for H_3^+ as an example and Ar^+ as a reference, to name a single example. This enables Dr. Dohnal to discuss the differences in the mechanisms to assist the recombination process. Equally the influence of the ortho and para nuclear spin configurations of H_3^+ behave differently, especially based on the number of resonant rotational states which are associated with the respective nuclear spin state. As it seems many more details can be disentangled in the future based on these first measurements. Here the depths of the recombination studies and all the details are impressing me very much.

I am also very fond of the stamina that the group in general and Petr Dohnal in particular have to go about mixtures of isotoplogues of H_3^+, because depending on the case only a comparatively small fraction of the ion cloud is associated with the species under consideration. This means that many cross-checking experiments are needed to prove that the conclusions really can be drawn from those measurements. Likewise, taking these measurements at different temperatures and as a function of the densities of the neutral collision partners, these are very cumbersome but also very relevant measurements. Thanks to the ability to address the specific isotopologue via spectroscopy, all these details can be unfolded in the studies which are documented in the original works attached to the thesis work. Overall, the additional understanding of the recombination processes, particularly under density conditions which are different from those in storage ring studies, is very good. The quality of the data, and the deep discussion of the consequences make this work very valuable. Again, this kind of work is turning into a trademark for the Prague group and Petr Dohnal in particular.

As mentioned above, I am also happy to see that the spectroscopic abilities of the new instruments are used for rather different studies. With particular interest I read the works where the spectroscopy of N_2^+ and N_2H^+ plays a central role. For N_2^+ it could be shown that the recombination of the ion with electrons studied is coming from vibrationally cold ions and the measured rates compare favorably with those values calculated for the vibrational ground state. But also, it has been found that N_2^+ ions in the first excited vibrational state recombine with electrons less efficiently than the ions in the vibrational ground state.

From the time evolution of several rotational states of N_2H^+ in the ground vibrational state it has been shown that the relative populations of different states of N_2H^+ are constant in SA-FALP plasma and that they are very close to their expected thermal populations. Likewise, such evolutions could be measured for the first vibrationally excited state of N_2H^+ (010). Its population turns out to be slightly higher than the kinetic temperature of the ion. Therefore, overall it could be assumed that the measured recombination rate coefficients belong to N_2H^+ with thermal populations of rotational and vibrational states. Again, the combination of spectroscopy and the accurate measurements of the FALP technique allows to pull out much more detail from the experiments than what was possible before.

Apart from the work in Prague Petr Dohnal visited a number of laboratories, collaborating with colleagues on related topics to his thesis work. In particular he reaches out to work on ion traps. Only little of this work is part of his thesis because he wanted to set a focus on the recombination work he conducted in recent years. Nevertheless, I am happy to see how he is interacting internationally such that his work is fertilized by input from other studies and he is working on his scientific independency and international reputation.

All in all, I think that Petr Dohnal advanced to a very mature scientist with the necessary degree of independence. His thesis work, especially the large set of original works fully justify his promotion as an academic teacher via his Habilitation. He will be an ambassador for his institute and Charles University Prague as a whole.

The (auto)plagiarism check (Turnitin system report) did not show scientific misconduct related to copying. Therefore, it is clear that the thesis is an original work with negligible overlap with existing literature written by the author. I would be happy to answer any open questions with respect to the evaluation of the scientific work of Dr. Petr Dohnal.

Sincerely yours

Prof. Dr. Stephan Schlemmer