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Opponent's report on the doctoral thesis:

"Studies of reactions of ions with water molecules in the gaseous phase for trace gas analysis"

By Michal LACKO

The doctoral work was dedicated to the studies of ion chemistry processes and techniques for trace gas analyses based on chemical ionisation mass spectrometry. The work of the candidate can be roughly divided in two parts: a) experimental work, which includes measurements on existing devices (of different types), their additional modifications and improvements and a comprehensive data analysis; b) development of complex numerical simulations used to understand, fit, and predict experimental findings. The interplay between these two parts, together with the theoretical understanding of the ion chemistry, should then improve the knowledge about limitations of the existing instruments for the trace gas analyses, and possibilities for further improvements regarding dominantly their sensitivity and selectivity. The work therefore could help development of fast and low-cost techniques with a variety of potential applications.

The doctoral thesis is written in English and includes two main parts: the doctoral thesis and the seven attachments (six reprints of papers and the KIMI Sim Software description). In the doctoral thesis, Chapter 1 contains quite detailed description and general introduction to the gas phase ion processes for trace gas analyses, description of different experimental techniques, the areas of applications and limitations, as well as the objectives of the present work. Chapter 2 describes the newly built device for gas chromatography, which makes a compromise between a high quality but slower gas chromatography and lower resolution but faster instruments allowing for a quick analysis of specific samples. Chapter 3 is dedicated to very detailed description of the newly developed package for numerical simulations of ion molecular reactions. Finally, the doctoral thesis also contains brief description and conclusions of each of the attached papers (Chapter 4).

I have the following questions and suggestions:

1. There are several schematic representations of different MS experimental setups given in the thesis (e.g. figures 2, 5, 7, 8). Figure 8 also reports the pumping speeds and pressure distributions along the flow direction.
 - a. It would be useful to comment on how this compares to the other standard setups presented earlier in the manuscript.
 - b. Could candidate shortly elaborate possible limitations (if any) to the sensitivity and selectivity, imposed by the cost and complexity of the instrument? For example, would the use of much stronger pumping capacity and therefore appropriate modifications of the limiting orifices and dimensions, lead to higher sensitivity?
2. On Page 50 of the manuscript, candidate states that changing over the reagent ion requires time, thus making impossible for a conventional PRT-MS to switch between reagent ions, which therefore limits its selectivity. Could this be briefly clarified, with some concrete numbers?
3. In Chapter 4.2. candidate briefly describes his work on ion chemistry of phthalates, starting with an appealing introduction about their global health risk. But then, it is not very clear at the end of the chapter how the present work could contribute to prevent his global risk? A summarizing statement with this respect would be useful.
4. The presence of the water vapor in the instrument and formation of hydronium clusters has been stressed frequently in the manuscript as an important effect that limits the sensitivity, and several solutions were proposed on how to reduce it. On the other hand, there have been long standing efforts to investigate water cluster under well-defined conditions. Could such an instrument be modified and used to investigate the properties of hydronium clusters, instead of trace gas analysis?

The PhD candidate is co-authoring five papers related to the doctoral thesis and the first author of three publications in leading international journals, confirming the quality and high scientific and applicative impact of the results. The doctoral thesis is written comprehensively and clearly. The candidate performed an imposing work and has obtained high quality scientific results. I am convinced that the candidate has a high ability for the high profile and independent scientific research. Therefore, I strongly recommend the presented doctoral work for the defence.

Gif sur Yvette, October 7th, 2022

Aleksandar Milosavljević, PhD