

Evaluation report on the theses of Ing. Erik Andris “Investigation of Non-Heme Iron-Oxo Intermediates in the Gas Phase”

Theses of Ing. Erik Andris “Investigation of Non-Heme Iron-Oxo Intermediates in the Gas Phase” sets a very ambitious goals to investigate iron-oxo species, including establishing the ion spectroscopy in the biomimetic chemistry and establishing the correlation between the gas phase and condensed phase reactivity of these species. Thesis is based on 3 papers in the very top journals (JACS and Angewandte); Ing. Andris is the first author on all of these publication and his contribution to all of them is major. It should be noted that during the course of his PhD study Ing. Andris has co-authored 16 papers (all of them in excellent journals) and he was the first author on 6 out of these 16 publications. It is thus evident that the Theses represents just a part of the work Ing. Andris has carried out during the PhD.

Contrary to the fact that the Theses is based only on 3 papers it is a very comprehensive work that is logically organized, well structured and clearly written. A good overview of experimental work on iron-oxo species and in particular on biomimetic iron-oxo species is presented in Chapter 1. Materials and methods relevant for the presented results are described in Chapter 2. Chapters 3 and 4 reports the main results obtained for iron(IV)-oxo and iron(III)-oxo species, respectively.

The goals stated in the Theses (and mentioned above) were clearly fulfilled with great success. Among large amount of novel and important data reported the main achievements of doctoral candidate include: (i) Establishing of infrared and visible photodissociation spectroscopies as highly valuable methods for the vibrational and electronic characterization of biomimetic iron complexes, respectively. (ii) Establishing of the correlation between gas and condense phase data of iron(IV)-oxo species. (iii) Discovering a way to assign the spin state based on the IR characteristics. (iv) Improving methods for generation of iron-oxo species. (v) Understanding of the reaction mechanisms involving iron-oxo species. These are really remarkable results that can be only achieved by a highly motivated researcher with excellent background in various fields of modern science, including organic chemistry, physical chemistry and chemical physics, analytical chemistry and quantum chemistry.

I have only one (minor) critical comment: at some places it is difficult quickly find a molecule/ion represented by bold numbers. There are defined in different figures at the Chapter 1 and in the text it is not always explicitly stated where to look for the definition. And some figures are duplicated, *e.g.*, Fig. 53 is the same as Fig. 12. Having just one figure defining all species repeatedly discussed in the text would be beneficial. But it is minor issue.

There is no need for more detail analysis of submitted Thesis; it is certainly one of the best doctoral thesis I have ever seen, it is an excellent work in the international standard and it clearly demonstrates the readiness of candidate to obtain the Ph.D. degree. It remains to congratulate him, his advisor and co-workers. Theses fulfill all the requirements and I recommend it to the defense committee for approval.

Below I have few question that should be considered mostly as curiosity questions:

Questions:

1. In part 2.6. Theoretical Calculations frequency scaling was described. It is stated that frequency scaling was not used for ZPVE calculations. Is there any particular reason for that?
2. Part of the DFT calculations were carried out with 6-311 type basis sets, why? These basis sets use the same exponents for s and p type AO which makes them less flexible than more modern basis sets.
3. It stated in section 2.6. that DFT is theoretically incorrect for the description of the systems with multi-reference character of the wave function and that they are used only qualitatively. This is true for almost all states except those with the highest spin. And it can lead to even qualitative disagreement with experiment since DFT is biased towards the highest spin states. Are there cases where reported relative energies of states calculated at the DFT level can be qualitatively wrong? Has a possibility to use so called symmetry-broken solution been considered for any of the system?

Prague, January 23rd 2019

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