Jerzy Haber Institute
of Catalysis and Surface Chemistry
Polish Academy of Sciences

HR EXCELLENCE IN RESEARCH

Review of doctoral dissertation

First and last name of the candidate: mgr Kinga Szkaradek

Title of doctoral dissertation: Theoretical studies on photoinduced charge and electron transfer processes in nucleobase pairs and their prebiotic precursors

Supervisors: prof. Robert W. Góra, prof. Jiri Sponer

Reviewer: prof. Tomasz Borowski, IKiFP PAN

1. Subject of the dissertation (whether the subject of the doctoral dissertation concerns issues important for the development of the discipline of chemical sciences)

The submitted dissertation is devoted to non-radiative deactivation processes of electronic excited states of canonical and alternative nucleobases and their pairs bound in the Watson-Crick manner. Due to the multitude of possible deactivation pathways and difficulties encountered in experimental studies of these processes, these are still poorly understood issues, although knowledge about them can significantly contribute to understanding the chemical origins of life on Earth and help explain differences in the observed photostability of the studied bases. The described studies fit into the mainstream of global research on the photochemistry of nucleic acids and their components, significantly contributing to the development of the discipline of chemical sciences.

2. Candidate's knowledge (assessment and justification of whether the doctoral dissertation presents the general theoretical knowledge of the person applying for the degree of doctor in the discipline of chemical sciences)

The dissertation is written in an extremely clear and mature manner. The introduction offers a concise but precise discussion of the theory of excitation and deactivation processes, computational methods used in the described studies, and an in-depth review of the literature on the subject. The cited literature includes as many as 288 items. The discussion of the results of own (computational) study is very often enriched by references to the results of research, both computational and experimental, described in the literature. Overall, the dissertation presents the candidate's general and in-depth knowledge in chemistry.

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3. Candidate's independence (assessment, together with justification, whether the doctoral dissertation demonstrates the ability to independently conduct scientific work by a person applying for the PhD degree)

I consider the selection of the systems studied, and the research methods used to study them to be very apt. The candidate first studied the relatively best known G-C complex, then studied the less well-known deactivation mechanisms for A-T and A-U pairs, and finally 14 pairs of alternative nucleobases, most of which were Terra Nova. The accuracy of the selected main research method (SCS-ADC(2)) was verified by confrontation with experimental results, where available, or with the results of more demanding computational methods, e.g. NEVPT2, CASPT2, EOM-CCSD. The research documented in the dissertation was conducted systematically and using appropriate research tools, the results were confronted with data available in the literature, and the conclusions drawn are confirmed by the results. In summary, the reading of the dissertation convinces that the candidate can conduct independent scientific work.

4. Originality of the dissertation (assessment with justification of whether the doctoral dissertation is an original solution to a scientific problem)

Most of the results presented in the dissertation are unprecedented in the scientific literature. The selection of the systems for the study (base pairs) and the applied computational methods allowed the candidate to test several important research hypotheses: a) that several alternative relaxation channels induced by charge transfer phenomena may exist simultaneously in the studied systems, and b) that non-absorbing (dark) $^{1}n\pi^{*}$ states may participate in non-radiative deactivation of the studied systems. The obtained results unequivocally confirmed the validity of these hypotheses and additionally provided information on the mechanisms of non-radiative deactivation processes in non-biological base pairs that could be prebiotic precursors of protonucleic acids. In summary, the dissertation is an original solution to an important scientific problem.

5. Questions and/or critical remarks to which the Reviewer expects the candidate to respond during the defense

I would kindly ask the candidate to discuss the potential role of triplet states in the processes of non-radiative deactivation and photodamage. Do triplet states deserve to be studied and if so, could the applied calculation methodology be extended to these states and their intersections with singlet states?

6. Other observations on the content or form of the dissertation

The dissertation is written with great care, the text is illustrated with clear and easy-to-understand drawings and diagrams, the number of linguistic errors is negligibly small. This is one of the best doctoral dissertations I have ever dealt with.

7. Final assessment

I, the undersigned, declare that the reviewed doctoral dissertation by M.Sc. Kinga Szkaradek meets the conditions specified in art. 187 of the Act of 20 July 2018 - Law on Higher Education and Science (Journal of Laws of 2018, item 1668, as amended) and I request the Discipline Council of Chemical Sciences of the Wrocław University of Science and Technology to admit M.Sc. Kinga Szkaradek to further stages of the proceedings regarding the award of the degree of PhD in the field of sciences in the discipline of chemistry.

I, the undersigned, request a distinction for the doctoral dissertation.

Justification for the request for distinction:

The significance of the undertaken research problem, the scope and quality of the conducted research, and the professional setting of the obtained results in the context of previous research described in the literature.

Kraków, 10.12.2024

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Date of review Signature of reviewer

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